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وقوانين الجامعة الأردنية وأنظمتها لطلبة الدكتوراة

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عنوان الرسالة / الاطروحة
Physical characterization of Poly(ethylene oxide) Doped with Sodium Iodide

أعلن بأنني قد التزمت بقوانين الجامعة الأردنية وأنظمتها وتعليماتها وقراراتها السارية المفعول المتعلقة بإعداد رسائل الماجستير والدكتوراة عندما قمت شخصيا" بإعداد رسالتي / اطروحتي ، وذلك بما ينسجم مع الأمانة العلمية المتعارف عليها في كتابة الرسائل والأطاريح العلمية. كما أنني أعلن بأن رسالتي /اطروحتي هذه غير منقولة أو مستلة من رسائل أو أطاريح أو كتب أو أبحاث أو أي منشورات علمية تم نشرها أو تخزينها في أي وسيلة اعلامية، وتأسيسا" على ما تقدم فإنني أتحمل المسؤولية بأنواعها كافة فيما لو تبين غير ذلك بما فيه حق مجلس العمداء في الجامعة الأردنية بإلغاء قرار منحي الدرجة العلمية التي حصلت عليها وسحب شهادة التخرج مني بعد صدورها دون أن يكون لي أي حق في التظلم أو الاعتراض أو الطعن بأي صورة كانت في القرار الصادر عن مجلس العمداء بهذا الصدد.

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Physical Characterization of Poly(Ethylene Oxide) Doped with Sodium Iodide

By

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Supervisor

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This Dissertation is Submitted in Partial Fulfillment of Requirements for the Doctor of Philosophy Degree in Physics

Faculty of Graduate Studies
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July, 2011

COMMITTEE DECISION

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DEDICATION

To whom is every thing in my life, Mama

To whom gave and still giving, Dad

To my wonderful husband, Mathhar

To all my brothers and sisters

To all my friends whom

I concern and love

My special dedication

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Physical Characterization of Poly(Ethylene Oxide) Doped with Sodium Iodide

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ABSTRACT

The optical, electrical, and thermal properties of prepared Poly(Ethylene Oxide) / Sodium Iodide (PEO/NaI) composites with different concentration: 0, 1, 2, 4, 6, 8, 10, 15% by weight were studied under various measuring conditions as filler content, optical wavelength, temperature, and applied field frequency.

Thin films of this electrolyte polymer composite were prepared by using the solution cast method with average thickness of 70 µm . Absorption and reflectance UV- spectra were collected by a spectrophotometer in wavelength range (300 nm-800 nm) . The optical data obtained were analyzed in terms of absorption formula for non-crystalline materials. The calculated values of optical energy gap and the width of the energy tails of the localized states exhibited NaI concentration dependence. The observed optical energy gap for neat PEO is about 2.6 eV, and decreases to a value of 2.36 eV for the film of 15 wt.% NaI content. The electrons transition mechanism is a direct one in k- space. It was found that the calculated refractive index and the dielectric constants of polymer electrolyte thin

films increase with NaI content. The overall dependence of the optical and dielectrical constants on NaI content is argued on the basis of the observed morphology. The effective – medium theory (EMT) model was fitted to describe the dependences of the dielectric constant on the NaI concentration.

The dependence of AC- electrical properties of PEO/NaI composites on frequency, temperature and filler content were studied using the powerful AC impedance technique. The impedance measurements were performed in frequency range 30kHz – 5MHz and temperature range (27 ºC - 60 ºC). It was found that the impedance values decrease with increasing frequency and temperature but increase with NaI concentration. The values of the dielectric constants, dielectric loss, and AC conductivity increase with increasing temperature and NaI content. Impedance, dielectric constant and AC- conductivity showed frequency, temperature and filler content dependence. The relaxation time and activation energy were determined as a function of temperature and filler concentration, respectively.

The thermal conductivities and thermal resistivities of PEO/NaI composites have been studied as a function of temperature. It was found that the thermal conductivity of electrolyte polymer composites increases slightly with both temperature and NaI concentration. Further more, the ratio between the observed thermal and electrical conductivities (Lorenz number) increases with NaI concentration. Some theoretical models were fitted to the observed electrical and thermals results, and it was found that the models fit is acceptiable.

CHAPTER ONE
INTRODUCTION

1.1 Polymer molecules

The molecules in polymers are gigantic in comparison to the hydrocarbon molecules will be discussed ; because of their size they are often referred to as **macromolecules.** Within each molecule, the atoms are bound together by covalent interatomic bonds. For carbon chain polymers, the backbone of each chain is a string of carbon atoms. Many times each carbon atom singly bonds to two adjacent carbon atoms on either side, represented schematically in two dimensions as follows: Each of the two remaining valence electrons for every carbon atom may be involved in side-bonding with atoms or radicals that are positioned adjacent to the chain. Of course, both chain and side double bonds are also possible. These long molecules are composed of structural entities called **repeat units,** which are successively repeated along the chain. The term **monomer** refers to the small molecule from which a polymer is synthesized, (A repeat unit is also sometimes called a mer. “Mer” originates from the Greek word **polymer** *meros,* which means part; the term **polymer** was coined to mean “many mers.”). Hence, monomer and repeat unit mean different things, but sometimes the term monomer or monomer unit is used instead of the more proper term repeat unit [Callister,2007].

1.2 Classification of polymers

The physical characteristics of a polymer depend not only on its molecular weight and shape but also on differences in the chemical structure of the molecular chains. There are many possible classifications of polymers :

(i) Classifications based on structure: linear, crosslinked, branched or network polymers. Figure 1.1 shows these types of polymer schematically. It should be noted that the real structures are three-dimensional, which is particularly important for networks. In recent years interest in more complicated structures than those shown in figure(1.1) has increased.

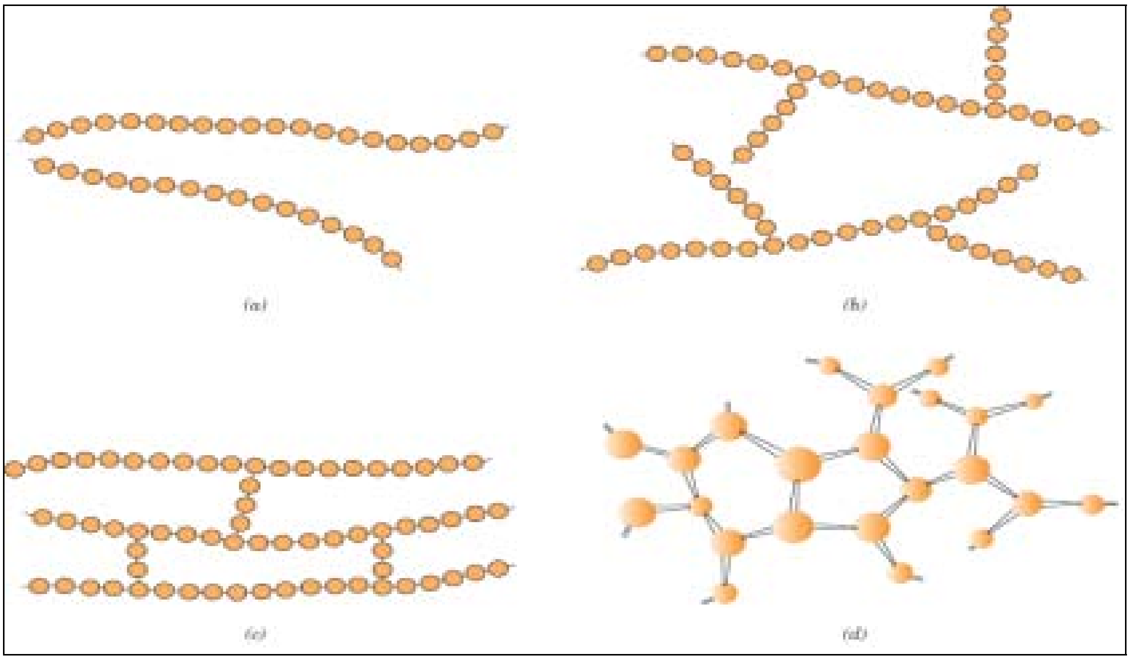


Figure (1.1): Schematic representations of (*a*) linear, (*b*) branched, (*c*) crosslinked, and (*d*) network (three-dimensional) molecular structures. Circles designate individual repeat units [Callister,2007].

Linear polymers are those in which the repeat units are joined together end to end in single chains. These long chains are flexible and may be thought of as a mass of spaghetti, as represented schematically in Figure (1.1 a), where each circle represents a repeat unit. For linear polymers, there may be extensive van der Waals and hydrogen bonding between the chains. Some of the common polymers that form with linear structures are

polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and the fluorocarbons [Callister,2007].

Polymers may be synthesized in which side-branch chains are connected to the main ones, as indicated schematically in Figure (1.1 b); these are fittingly called **branched polymers.** The branches, considered to be part of the main-chain molecule, may result from side reactions that occur during the synthesis of the polymer. The chain packing efficiency is reduced with the formation of side branches, which results in a lowering of the polymer density.Those polymers that form linear structures may also be branched. For example, high density polyethylene (HDPE) is primarily a linear polymer, while low density polyethylene (LDPE) contains short chain branches [Callister,2007].

In **crosslinked polymers,** adjacent linear chains are joined one to another at various positions by covalent bonds, as represented in Figure (1.1, c). The process of crosslinking is achieved either during synthesis or by a nonreversible chemical reaction. Often, this crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber elastic materials are crosslinked; in rubbers, this is called vulcanization.

Multifunctional monomers forming three or more active covalent bonds, make three-dimensional networks (Figure 1.1, d) and are termed **network polymers.** Actually, a polymer that is highly crosslinked may also be classified as a network polymer. These materials have distinctive mechanical and thermal properties; the epoxies, polyurethanes, and phenol-formaldehyde belong to this group. Polymers are not usually of only one distinctive structural type. For example, a predominantly linear polymer might have limited branching and crosslinking [Callister,2007].

(ii) Classifications based on properties: (thermo)plastics, rubbers (elastomers) or thermosets.

Thermoplastics form the bulk of polymers in use. They consist of linear or branched molecules and they soften or melt when heated, so that they can be moulded and remoulded by heating. On cooling they may form a glass (a sort of 'frozen liquid') below a temperature called the glass transition temperature, T_g, or they may crystallise. If they crystallize they do so only partially, the rest remaining in a liquid-like state which is usually called amorphous, but should preferably be called non-crystalline. In some instances, they form a liquid-crystal phase in some temperature Regions [Young,1981].

Rubbers, or elastomers, are network polymers that are lightly crosslinked and they are reversibly stretchable to high extensions. When unstretched they have fairly tightly randomly coiled molecules that are stretched out when the polymer is stretched. This causes the chains to be less random, so that the material has a lower entropy, and the retractive force observed is due to this lowering of the entropy. The cross-links prevent the molecules from flowing past each other when the material is stretched. On cooling, rubbers become glassy or crystallise (partially). On heating, they cannot melt in the conventional sense, i.e. they cannot flow, because of the cross-links [Young,1981].

Thermosets are network polymers that are heavily cross-linked to give a dense three-dimensional network. They are normally rigid. They cannot melt on heating and they decompose if the temperature is high enough. The name arises because it was necessary to heat the first polymers of this type in order for the cross-linking, or curing, to take place. The term is now used to describe this type of material even when heat is not required for

the cross-linking to take place. Examples of thermosets are the epoxy resins, such as Araldites, and the phenol- or urea-formaldehyde resins [Young,1981].

1.3 The chemical nature of polymers

Polymer is used to mean a particular class of macromolecules consisting, at least to a first approximation, of a set of regularly repeated chemical units of the same type, or possibly of a very limited number of different types (usually only two), joined end to end, or sometimes in more complicated ways, to form a chain molecule. If there is only one type of chemical unit the corresponding polymer is a homopolymer; if there is more than one type it is a copolymer [Bower,2002].

It should be noted that the term monomer or monomer unit is often used to mean either the chemical repeat unit or the small molecule which polymerises to give the polymer. These are not always the same in atomic composition, as will be clear from what follows, and the chemical bonding must of course be different even when they are. The simplest polymers are chain-like molecules of the type

—A—A—A—A—A—A—A—A—A—A—A—A—A—

where A is a small group of covalently bonded atoms and the groups are covalently linked. The simplest useful polymer is polyethylene

—CH2—CH2—CH2—CH2—CH2—CH2—CH2—CH2—

The chemical structures of the repeat units of some common polymers are shown in figure (1.2).

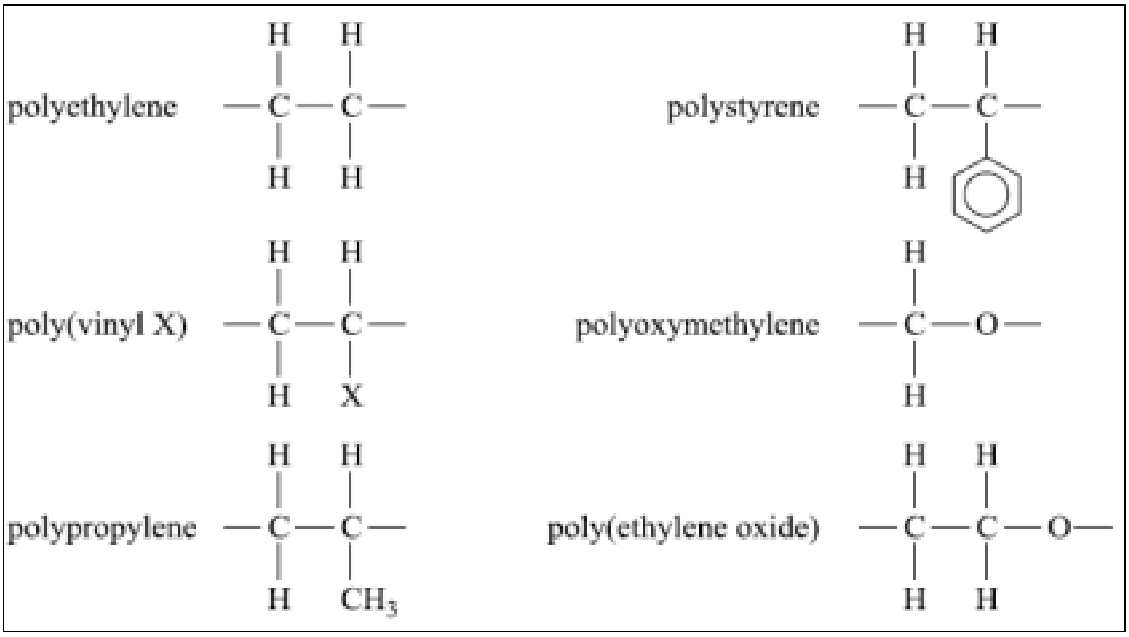


Figure (1.2): Structures of the repeating units of some common polymer [Bower,2002]

1.4 Physical properties of polymers

Physical properties of polymers include:

1. Degree of polymerization - The number of structural units in a polymer chain.
2. Molar mass distribution - The relationship between a polymer fraction and the molar mass of that polymer fraction.
3. Branching - Polymer chains extending from the main polymer backbone chain.
4. Stereoregularity or tacticity - the isomeric arrangement of functional groups on the backbone of carbon chains.
5. Crystallinity - as well as the thermal phase transitions:

6. T_g, glass transition temperature, and Tm, melting point (for thermoplastics).

7. The enthalpy and heat of fusion.

1.5 Composites

A composite is composed of two (or more) individual materials, metals, ceramics, and polymers. The design goal of a composite is to achieve a combination of properties that is not displayed by any single material, and also to incorporate the best characteristics of each of the component materials. A large number of composite types exist that are represented by different combinations of metals, ceramics, and polymers. Furthermore, some naturally-occurring materials are also considered to be composites—for example, wood and bone.

One of the most common and familiar composites is fiberglass, in which small glass fibers are embedded within a polymeric material (normally an epoxy or polyester). The glass fibers are relatively strong and stiff (but also brittle), whereas the polymer is ductile (but also weak and flexible). Thus, the resulting fiberglass is relatively stiff, strong, flexible, and ductile. In addition, it has a low density.

Another of these technologically important materials is the “carbon fiber reinforced polymer” (or “CFRP”) composite—carbon fibers that are embedded within a polymer. These materials are stiffer and stronger than the glass fiber-reinforced materials, yet they are more expensive. The CFRP composites are used in some aircraft and aerospace applications, as well as high-tech sporting equipment (e.g., bicycles, golf clubs, tennis rackets, and skis/snowboards). The following are some of the reasons why composites are selected for certain applications:

- High strength to weight ratio (low density high tensile strength)
- High creep resistance
- High tensile strength at elevated temperatures

- High toughness

Typically, reinforcing materials are strong with low densities while the matrix is usually a ductile, or tough, material. If the composite is designed and fabricated correctly, it combines the strength of the reinforcement with the toughness of the matrix to achieve a combination of desirable properties not available in any single conventional material. The downside is that such composites are often more expensive than conventional materials. Examples of some current application of composites include the diesel piston, brake-shoes and pads, tires and the Beech craft aircraft in which 100% of the structural components are composites.

The strength of the composite depends primarily on the amount, arrangement and type of fiber (or particle) reinforcement in the resin. Typically, the higher the reinforcement content, the greater the strength. In some cases, glass fibers are combined with other fibers, such as carbon to create a "hybrid" composite that combines the properties of more than one reinforcing material. In addition, the composite is often formulated with fillers and additives that change processing or performance parameters.

Three types of composites are:

- Particle-reinforced composites
- Fiber-reinforced composites
- Structural composites

In designing composite materials, scientists and engineers have ingeniously combined various metals, ceramics, and polymers to produce a new generation of extraordinary materials. Most composites have been created to improve combinations of mechanical characteristics such as stiffness, toughness, and ambient and high-temperature strength.

1.6 Polymer additives (Filler)

Foreign substances called *additives* are intentionally introduced to enhance or modify many of mechanical, chemical, and physical properties, and thus render a polymer more serviceable. Typical additives include for example, filler materials. **Filler** materials are most often added to polymers to improve tensile and compressive strengths, abrasion resistance, toughness, dimensional and thermal stability, and other properties. Materials used as particulate fillers include wood flour (finely powdered sawdust), silica flour and sand, glass, clay, talc, limestone, and even some synthetic polymers.

Particle sizes range all the way from 10 nm to macroscopic dimensions. Polymers that contain fillers may also be classified as composite materials. Often the fillers are inexpensive materials that replace some volume of the more expensive polymer, reducing the cost of the final product [Callister,2007].

1.7 Sodium Iodide (NaI)

Sodium iodide is a white, crystalline salt with chemical formula NaI. It is a kind of scintillation crystal with good properties .It has a very high luminescence efficiency with melting point 661°C. It is used in radiation detection, treatment of iodine deficiency, nuclear medicine and in many other applications, such as x-ray detectors with high

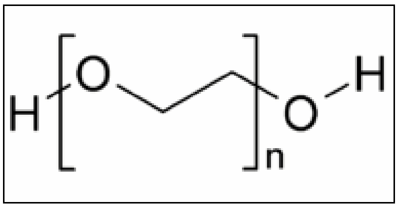
spectrometric quality. Sodium iodide crystallizes in the fcc space group a= 6.479A° ,with four sodium and four iodide atoms per unit cell.[S. Neyertz, D. Brown, J. Thomas, 1995].

Table (1.1) Physical properties of Sodium iodide [www.Wikipedia.org]
*** http:// www.amcrys-h.com/ crystals.htm**

Chemical Formula	NaI
Appearance	White granular or colorless crystals
Odor	Odorless.
pH	8 - 9.5
Boiling Point	1304 °C (1 atm.)
Melting Point	661 °C
Density	3.67 g/cm^3
Solubility in water	178.8 g/100 mL (20 °C) 184 g/100 mL (25 °C) 294 g/100 mL (70 °C)
Solubility	soluble in ethanol and acetone
Structure (Coordination geometry)	Octahedral
Molar mass	149.894 g/mol
*Refractive index	1.85
Heat Capacity	0.347 J/g K
*Dielectric constant	7.28

1.8 Polyethylene Oxide (PEO)

Polyethylene Oxide (PEO) is a nonionic homopolymer of ethylene oxide, represented by the formula (-CH_2CH_2O-)*n*., in which *n* represents the average number of oxy- ethylene groups and its structure is:



Poly(ethylene oxide) (PEO), is a synthetic polyether that is readily available in arrange of molecular weights (Mw). Material with Mw <100,000 g/mol are usually called Poly (ethylene glycol) PEG, while higher molecular weight polymer are classified as PEO. These polymers are soluble in water as well as in many organic solvents (e.g., methylene chloride, ethanol, toluene, acetone, and chloroform). PEOs are white solids with melting point proportional to their molecular weights. The interesting properties of PEO are its relatively low melting point 65°C, good structural integrity, low glass transition temperatures -65 °C, which permits ion transport at ambient temperature, low toxicity. On other hand, PEO is the most popular polymer used, due to its high solvating power with metal ions, good process ability and outstanding mechanical properties, it has a lot of trade names (Alathen, Fortiflex, Zendel) [www.Wikipedia.org].

Poly (ethylene oxide) is a familiar example of the thermoplastic polymers, and these can be further sub- divided into amorphous and crystalline polymers structures.

Table (2.2): Physical properties of Poly (ethylene oxide) (PEO)
***[www.Wikipedia.org]. ** http://www.polymerdata.com**

*Appearance	white powder
*Melting Point (molecular weight >(20 000))	65°C
** Refractive index	1.456
** Dielectric constant	4.5
glass transition temperatures (T_g)	-65 °C

Most polymeric materials are poor conductors of electricity because of the unavailability of large numbers of free electrons to participate in the conduction process. So a great attention has been focused on enhancing their electrical conduction and improving their properties [Callister, 2007]. Polymers exhibit a variety of electrical properties reflecting their structure and molecular motion. Electrical properties can be tailored to a specific requirement by the addition of suitable dopant materials]. In PEO polymer electrolyte cations of ionic salt are coordinated with the ether oxygen of PEO. Change in chemical composition can vary the physical properties of the electrolyte. The ion conduction mechanism is assumed to be cation mobility, in which polymer chain motion plays a significant role. The concentrations of charge carriers are important, which is the function of salt concentration in the polymer. [Kumar,2006].

1.9 Crystal structure of poly (ethylene oxide) /sodium iodide complex

The crystal structure of poly (ethylene oxide) /sodium iodide (PEO/NaI) complex, a highly ionic conductor, was determined by the X- ray diffraction method. The cell constant are a= 18.15 Aº, b= 8.14 Aº, c (chain axis)= 7.98 Aº and there are 12 monomer units (two chains) and four NaI ion pairs in the unit cell. The NaI chain is coiled round by the helical PEO chain that makes a fiber period of 7.98 Aº with six EO unites , Figure (1.3). Each Na^+ ion is coordinated by three polymer oxygen atoms and two I^- ions, and these ions are linked alternately. Wright *et, al*. reported that the conductivity of the NaI complex depends on the morphology of the system. The crystalline part, crystal boundaries and the amorphous part must exhibit distinguishable behaviors in ionic conduction. Information on structures of many complexes is indispensable to clarify the relation between structure and conductivity of PEO- alkali- metal salt system [Yoso Chatani and Sigeru Okamura, 1987].

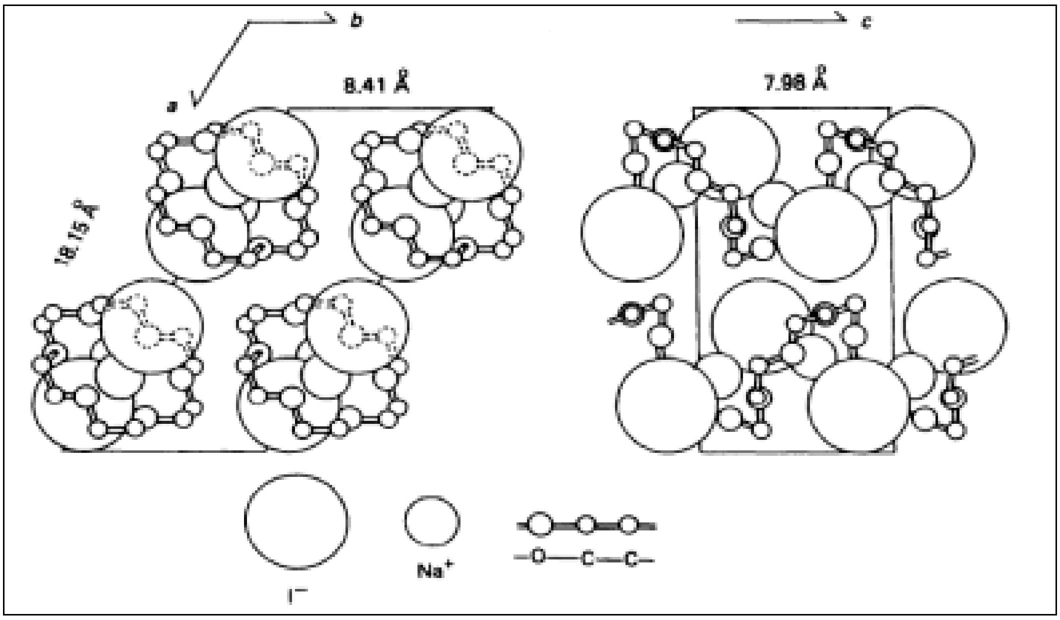


Figure (1.3): Crystal structure of PEO/NaI complex

1.10 Previous Work

Some of the reported research works dealing with the physical properties of polymer composites are:-

- Kostopoulos. D. et. al, (1980) studied the mass thermal diffusion and electrical conduction in NaI. They measured the diffusion coefficient for the cation and anion motion at high temperatures and the DC conductivity. They found that the results are as expected from low temperature up to 630°C; and at about 30°C below the melting point a strong upward curvature appears in all plots of the diffusion coefficient versus the temperature reciprocal. They attributed this deviation from linearity to an harmonic effects on the defect parameters during the formation and migration processes.

- Wright P. (1995), studied the ionic conduction in thin films of Polyether – Alkali – metal salt complexes. He reported states of ionic association, ionic conductivity, and macromolecular organization of these complexes leading to better understanding of the ionic transport mechanism in salt – PEO polymeric system, and concluded that the amorphous phase is the principal pathway for ionic mobility in PEO polymer.

- Stolwijk et. al, (2006), investigated the effects of temperature and salt concentration on mass and charge transport in the PEO – NaI polymer

electrolyte system. It was found that both the enthalpy and entropy of ion pair formation decrease with increasing salt concentration. This indicates that the state coordination between cations and polymer chain segments correlates with the number of available oxygen atoms per cation. The charge diffusivity of Na and iodine showed systematic dependence on both temperature and salt concentration based on the occurance of neutral ion pair in addition to charged single cations and anions.

- A. Abu-Jamous and A. Zihlif, (2009), studied the Ac-impedance behavior of PEO/iodine thin films as a function of frequency, temperature and iodine content. They observed an anomalous ac conductivity dependence on iodine content. Also, they investigated the dielectric properties and the thermal activation energy of the prepared composites.

- Sengwar et. al, (2003) studied the dielectric properties of iodine doped poly (vinyl alcohol) films, and found anomalous variation in conductivity with increasing the I_2 concentration. They reported that the variations in the electrical behavior are due to complex formation of PVA molecules with iodine.

- Reddy et. al, (1992) studied the effect of iodine on electrical conduction in cellulose acetate polymer films. They found that the conductivity in the sample

increases with increasing I_2 concentration up to 0.5 wt%. Above this concentration the conductivity was found to decrease. Also, they found that the thermal activation energy has the same concentration dependence.

- Mehandra and Chard (1983) studied the effect of iodine on depolarization behavior of (PVF) films. They found that when the concentration of I_2 was increased beyond 0.5 wt%, the conductivity decreases owing to the decrease of the mobility of the charge carries produced by I_2 complex formation in the PVF films and trapped carrier density.

- Ragavendran et. al, (2004) studied the AC behavior of plasticized PEO based solid polymer electrolyte. They attributed the high conductivity of PEO/Lithium to the enhanced mobility of the ions and reduced energy barrier to the segmental motion of Lithium ions in the PEO matrix.

- Fanggao et. al, (1996) performed electrical impedance measurements of PEO under different applied frequency, hydrostatic pressure, and temperature. They reported the effect of frequency, temperature and pressure on the dielectric parameters of PEO polymer. They related the observed variation in the dielectric properties to the viscoelastic relaxtions of glass / rubber transitions. Also, from the pressure effect, they determined the shifts of the peaks and activation volume of the occurred relaxations.

- Lewis and Taylor (1972) studied the electrical conduction in Iodine-doped polyethylene. They found that I_2 diffuses through polyethylene forming donor-acceptor complexes. They determined the iodine diffusion constant and the number of possible charge transfer, and confirmed Swan model for the mechanism of enhanced conduction through neutral iodine diffusion of I_2 into interstitial positions in polyethylene.

- Mohan et. al, (2007) studied the electrical and optical properties of sodium/PEO electrolyte films casted from solution. The electrical conductivity was measured as a function of temperature and dopent concentration. The optical absorption was studied in UV-radiation. They determined the band gaps for these films as : 4.54 and 3.44 for direct and indirect electron transitions. The conductivity is found to increase with increase of temperature in all composites.

1.11 Present Work

The objective of the research project presented in this dissertation is to investigate the optical, thermal and AC electrical properties of the prepared poly(ethylene oxide)/ sodium iodide (PEO/NaI) composites.

The present study includes the following aspects:

1. Composites preparation: composite of NaI (filler) and PEO (matrix) were prepared with different concentrations.
2. Studying the optical properties of PEO/NaI composites in UV-visible wavelength range (300nm-800nm) for different NaI concentration.
3. Studying the dependence of the thermal properties on temperature in the range of (27^0 C-60^0 C) for different NaI concentrations.
4. Studying the AC electrical conductivity as a function of frequency in the range (30 kHz - 5 MHz) and temperature in the range (27^0 C- 60^0C) for different NaI concentration.
5. Determination of some physical properties of the prepared composites like the optical energy gap, energy tails, refractive index, thermal conductivity, impedance dielectric constant, AC conductivity and Lorenz number.
6. Attempts to fit some theoretical models to describe the property behavior.

CHAPTER TWO
THEORETICAL BACKGROUND

The theoretical background is needed to discuss the optical electrical and thermal properties of PEO/NaI composites under different measuring conditions applied field frequency, temperature, and filler concentration.

2.1 Optical Properties

When a material is illuminated with light there are several processes that can occur as a result of the interaction between the light and the material. Some light may be lost and the energy transformed into heat in which case it is absorbed. Some, however, may pass through without loss, i.e. transmitted, or scattered back from the surface of the material, i.e. reflected.

Absorption is the basic mechanism needed for the detection of light, reflection is required for mirrors and transmission is essential for optical components such as lenses and prisms. It is therefore of fundamental importance to understand how these phenomena arise.

The basic interaction which gives rise to all optical properties is that between the electromagnetic (E.M.) field of the light (particularly the electric vector) and the charges contained in the material. This is always the basic process but its precise form depends very much upon the nature of charges and their distribution, that is whether they are electronic or

ionic, whether they are free as in a metal or bound as in a semiconductor or insulator [Lovell; Avery; 1977].

The electromagnetic spectrum covers a broad range of frequencies from short wave gamma radiation to long radio waves. It propagates through space with the speed of light (c) which equals the product of their frequency ν and wavelength λ [Jastrzebski, 1977].

$$c = \lambda\nu \tag{2.1}$$

The degree of interaction of the electromagnetic waves with matter depends on their wavelength and frequency and on the characteristic properties of materials. When light strikes a body, it can undergo one of the three processes. For a given wavelength λ, incident radiation may be reflected, absorbed, or transmitted, depending on the wavelength of the incident radiation and the properties of the substance.

2.1.1 Absorption of light

In the absorption process, a photon of known energy excites an electron from a lower energy state to a higher one. By studying the transmitted radiation, it can often be decided on possible transitions an electron can make. The fundamental absorption manifests itself by a rapid rising in absorption, known as the absorption edge. This can be used to determine the optical energy gap and may best be explained based on band-to-band or band-to-exciton transition. Absorption is expressed in terms of the coefficient α (ω), defined as the relative decrease rate in light intensity.

If light of intensity I_0 is incident on a slab of thickness x, and light of intensity I is transmitted, the amount of the absorbed intensity is proportional to the sample thickness, and the differential absorption can be expressed as

$$dI(\lambda) = -\alpha I(\lambda) dx \qquad (2.2)$$

, which upon integration from 0 to x gives the exponential law of absorption, the basic working relationship

$$I(\lambda) / I_0(\lambda) = \exp[-\alpha x] \qquad (2.3)$$

, where α is the absorption coefficient, defined as the relative decrease rate in light intensity characteristic for a particular solid or medium, and it is a function of the wave length. So, the intensity of the transmitted portion of light I (λ) is given by

$$I(\lambda) = I_0(\lambda) \exp[-\alpha(\lambda) x] \qquad (2.4)$$

Several absorption mechanisms are active in semiconductors: intrinsic or fundamental absorption, free carrier absorption, internal-band absorption, impurity absorption, lattice absorption, exciton absorption and plasma absorption [Kireev, 1978].

Whenever absorption is involved the energy carried by the E.M. wave becomes important, and for these situations it is necessary to adopt the quantum approach and to consider the light as consisting of many individual particle-like packets of energy, i.e. photons. Each photon possesses an energy (E) defined as [Lovell, 1977]

$$E = h\nu = hc/\lambda = \hbar\omega \qquad (2.5)$$

where ($\omega = 2\pi\nu$) is the photon frequency, and ($\hbar = h/2\pi$) is Plank's constant.

Absorption can occur between occupied and unoccupied states of energy. If these states are separated by an energy ΔE, absorption will only occur provided the photon energy equals ΔE (see Figure (2.1)), i.e.

$$\nu = \Delta E / h \qquad (2.6)$$

$$\lambda = h c / \Delta E$$

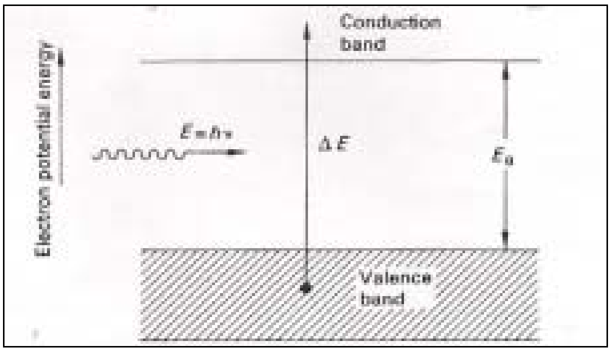


Figure (2.1): The absorption of a photon by a valence electron [Lovell, 1977].

This fundamental absorption is characterized by a very broad spectrum since the broad energy band give a wide choice of transitions. The most important transitions for nonmetallic materials are those between the valence band and the conduction band. Every material is characterized by an energy gap E_g so that a minimum photon energy exists which will give excitation resulting in absorption. From equation (2.6) this leads to a critical wavelength;

$$\lambda = h c / E_g \qquad (2.7)$$

at which there will be sharp edge in the absorption spectrum. To the long wavelength side of this edge the material will be transparent [Lovell, 1977].

Absorption of a photon of light may occur by the promotion or excitation of an electron from the nearly filled valence band, across the band gap, and into an empty state within the conduction band. A free electron in the conduction band and a hole in the valence band are created. The energy of excitation ΔE is related to the absorbed photon

frequency. These excitations with the accompanying absorption can take place only if the photon energy is greater than that of the band gap —that is, if ($h\nu > E_g$). (Callister, 2007).

When light penetrates a semiconductor or insulator, a different type of absorption processes takes place. The most important absorption process is the fundamental (intrinsic) absorption; analysis of this absorption provides us with information about the energy gap and its magnitude. The variation of the absorption coefficient (α) with the incident photon energy ($\hbar\omega$), in this type of absorption, was predicted by several theoretical models [Al-Ani& Hogarth, 1993].As a result of these models, the general behavior of the absorption coefficient (α) with photon energy is represented by the curve which shows three main regions:

1) In the low photon energy region of the curve the absorption coefficient (α) decreases exponentially with decreasing photon energy and Urbach tail is observed, in this region, the absorption coefficient (α) obeys the empirical Urbach rule given as [Sbeih and Zihlif ,2009].

$$\alpha = \alpha_0 \exp\left[(\hbar\omega - E_1)/\Delta E\right] \qquad (2.8)$$

where α_0 is a constant with dimension of cm^{-1}, E_1 is another constant , and ΔE is the width of the Urbach tail, which is a measure of the disorder of the material.[Elliot,2000].

2) Intermediate absorption region in which the absorption coefficient (α) ranges 10^3-10^4 cm^{-1}, and varies exponentially with $\hbar\omega$. This behavior of α can still be predicted by equation (2.8).

3) At high photon energy, an interband absorption (transition of excited electrons from the valence band to the conduction band) occurs. The value of the absorption coefficient (α) in this region is in the range (10^4-10^6) cm^{-1}. Interband transition can take place via two possible mechanisms: direct transition and indirect one. [Ziadat and Zihlif, 2005].

Band-to-band absorption or fundamental absorption of radiation occurs due to the photo-excitation of an electron from the valence band to the conduction band. Thus, absorption of a photon creates an electron in the conduction band and a hole in the valence band and requires the energy and momentum conservation of the excited electron, hole, and photon. In crystalline solids, as the band structures depend on the electron wavevector k, there are two types of band -to-band absorption corresponding to direct and indirect transitions. In contrast, in amorphous solids, where no longer-range order exists only direct transitions are meaningful. [Elliot, 2000].

2.1.2 Direct transition

A direct transition is a photoexcitation process in which no phonons are involved. In direct-gap materials (e.g. crystalline GaAs), electronic transitions occur for $\hbar\ \omega \geq E_g$ (neglecting the effect of the photon wave vector); hence, the optical absorption spectrum of such materials increases discontinuously at $\hbar\omega = E_g$ as shown in Figure (2.2), and an extrapolation of the absorption curve to zero absorption yields an estimate for E_g.

As the photon momentum is negligible compared with the electron momentum when the photon is absorbed to excite an electron from the valence band (**V_B**) to the conduction band **(C_B)**, the electron's **k-**vector does not change. A direct transition in Figure (2.2) is a vertical transition from an initial energy E and wavevector k in the V_B to a final energy ***E`*** and wavevector ***k`*** in the **C_B** where k`= k, where (k=| **k**|). The energy ($E^{`}$-$E_C$) is the kinetic

energy $(\hbar\ k)^2/\ (2m^*_e)$ of the electron with the effective mass m^*_e, and $(E_r\text{-}E)$ is the kinetic energy $(\hbar\ k)^2/\ (2m^*_h)$ of the hole left behind in the $\mathbf{V_B}$. The ratio of the kinetic energies of the photogenerated electron and hole depends inversely on the ratio of their effective masses. The absorption coefficient α is derived from the quantum mechanical transition probability from E to $E^{`}$, the occupied density of states at E in the **VB** from which electrons are excited, and the unoccupied density of states in the $\mathbf{C_B}$ at $E+hv$. The α depends on the joint density of states at $E+hv$, and we have suitably integrate this joint density of states [Singh,2006]. Near the band edges, the density of states can be approximated by a parabolic band and the absorption coefficient α is obtained as a function of the photon energy as [Elliot, 2000]:

$$\alpha\hbar\omega = \left(\frac{4\pi\sigma_0}{nc\Delta\mathrm{E}}\right)(\hbar\omega - \mathrm{E}_{opt})^r \qquad (2.9)$$

where σ_0 is the DC conductivity, n is the refractive index of the sample, c is the speed of light, r is an index, and ΔE is a measure of the width of the tails in localized states in the band gap.

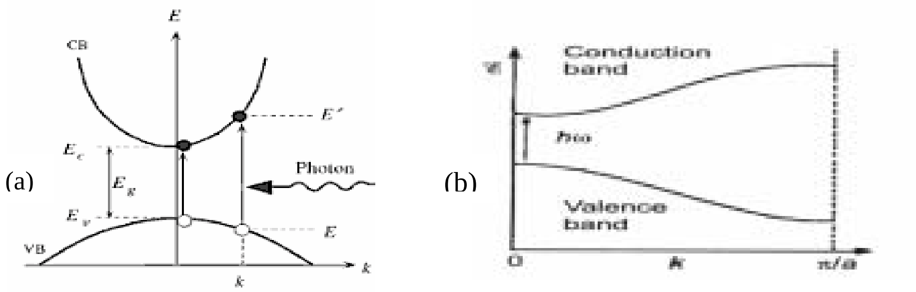


Figure (2.2): (a) Direct transition of electron. [Singh, 2006](b) vertical, crystal-momentum-conserving direct transition occurring at the minimum band gap, $\mathbf{E_g}$ [Elliot,2000].

2.1.3 Indirect Transition:

If the bottom of the conduction band E_c occupies the position whose value of k-wavevector differs from that for the top of the valence band E_V, Figure (2.3), then a vertical electronic transition, involving only a photon cannot directly connect the two electronic states, a photon does not possess enough momentum to ensure conservation of momentum for such transition. A number of possible additional processes, however, can provide the necessary extra momentum to affect an indirect transition. The most general of these involves phonons. A phonon can be either emitted or absorbed with enough (but small) energy ($\hbar\omega_p$) to cause the electron transition to the conduction-band minimum, i.e. the conservation of energy now reads:

$$\left.\begin{aligned} E_e &= E_p + \hbar\omega \pm E_{phon} \\ P_e &= P_p + P_{phot} \pm P_{phon} \end{aligned}\right\} \qquad (2.10)$$

Where E_e, E_p, E_{phon} are the energy of electron, hole, and phonon, respectively, and P_e, P_p, P_{phot}, and P_{phon}, are the momenta of electron, hole, photon, and phonon, respectively. The plus sign refers to the process involving phonon absorption and the minus sign refers to the process involving phonon emission.

Theoretical calculation of the absorption coefficient (α) for indirect transition is given by [Fukuda, 1999; Peled, 2003]:

$$\alpha\hbar\omega \sim [\, \hbar\omega - (E_g \pm E_{phon})\,]^2 \qquad (2.11)$$

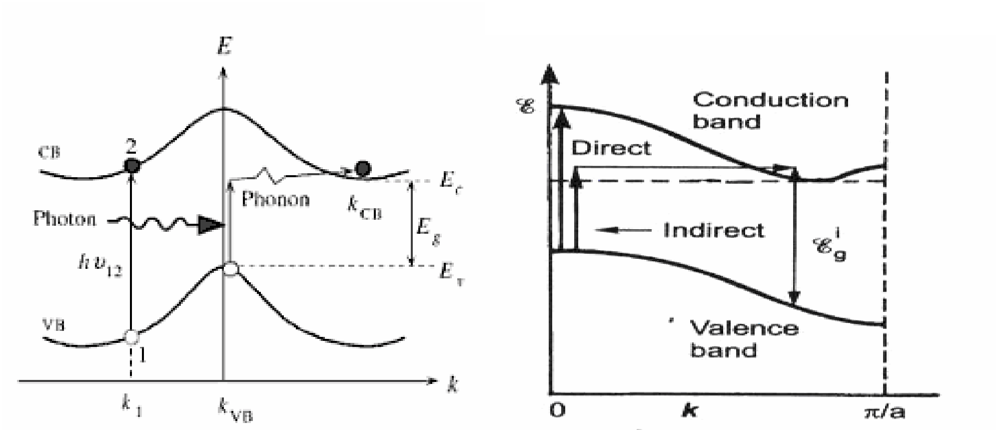


Figure (2.3): Indirect transition of electron. [Singh, 2006]

From the above discussion we can conclude that in crystalline solids, as the band structures depend on the electron wavevector k, there are two types of band -to-band absorption corresponding to direct and indirect transitions. In contrast, in amorphous solids, where no longer-range order exists only direct transitions are meaningful. [Singh, 2006].

2.2 Electrical Properties

Consideration of the electrical properties of materials is often important when materials selection and processing decisions are being made during the design of a component or structure. The electrical behaviors of the various materials are diverse. Some need to be highly electrically conductive (e.g., connecting wires), whereas electrical insulativity is required of others (e.g., the protective package encapsulation).

Electrical properties of polymers, elastomers, composites and films are important in a wide range of industries including automotive, aerospace, building products, marine, packaging

and consumer goods. Electrical tests, in general, are measurements of the resistance, conductivity or charge storage either on the surface or through the plastic material.

Electrical conductivity or specific conductivity is a measure of a material's ability to conduct an electric current. When an electrical potential difference is placed across a conductor, its movable charges flow, giving rise to an electric current.

Sometimes, electrical conductivity σ is used to specify the electrical character of a material. It is simply the reciprocal of the resistivity, or

$$\sigma = 1 / \rho \qquad (2.12)$$

, and it is indicative of the ease of with which a material is capable of conducting an electric current. The units of σ are reciprocal ohm-meters [$(\Omega.\ m)^{-1}$, or mho/m].

Solid materials exhibit an amazing range of electrical conductivities, extending over 27 orders of magnitude; probably no other physical property experiences this breadth of variation.

In fact, one way of classifying solid materials is according to the ease with which they conduct an electric current; within this classification scheme there are three groupings: conductors, semiconductors and insulators. If the solid is characterized by a partially filled valence band at 0 kelvin, it is a conductor. If the valence band is completely filled at 0 kelvin, the solid is either a semiconductor or an insulator. The distinction between a semiconductor or an insulator is based on the magnitude of the energy gap.

Metals are good conductors, typically having conductivities on the order of 10^7 $(\Omega.\ m)^{-1}$. On the other extreme insulating materials have very low conductivities, ranging 10^{-10} - 10^{-20} $(\Omega.\ m)^{-1}$, these are electrical insulators. Materials with intermediate conductivities,

generally from 10^{-6} to 10^{4} $(\Omega.\ m)^{-1}$, are termed semiconductors [Callister, 2007]. See the following figure.

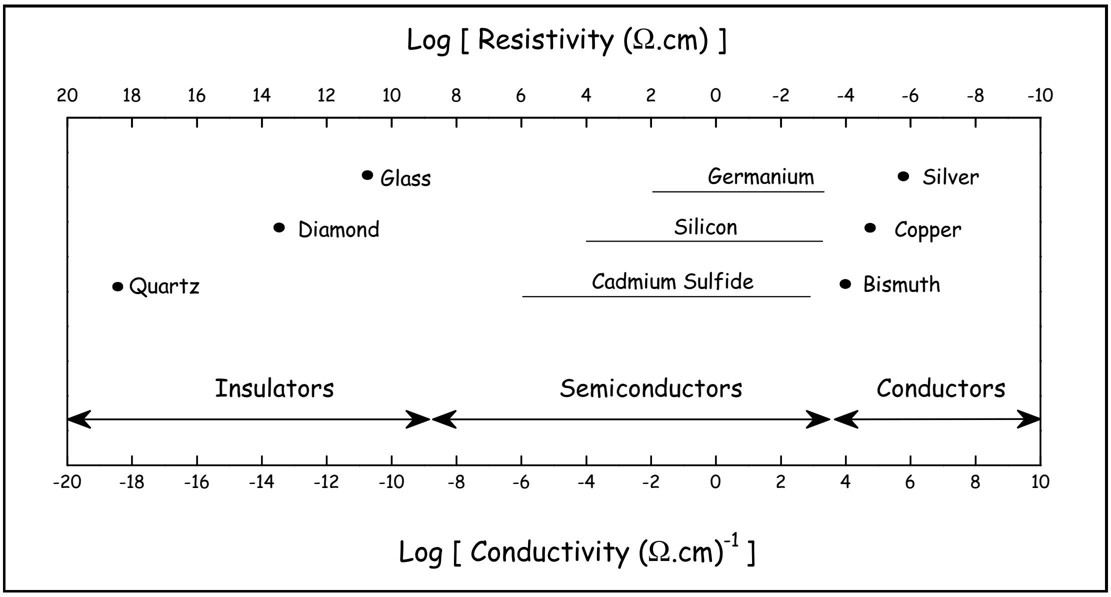


Figure (2.4): The electrical conductivity for different materials [Hummel,1993].

2.2.1 Energy band structure

The enormous variation in electrical conductivity of metals, semiconductors, and insulators may be explained qualitatively in terms of their energy bands.

Energy bands consisting of a large number of closely spaced energy levels exist in crystalline materials. The bands can be thought of as the collection of the individual energy levels of electrons surrounding each atom. The wavefunctions of the individual electrons, however, overlap with those of electrons confined to neighboring atoms. The Pauli exclusion principle does not allow the electron energy levels to be the same so that one obtains a set of closely spaced energy levels, forming an energy band [Callister, 2007].

The electrical properties of a solid material are a consequence of its electron band structure, that is, the arrangement of the outer most electron bands and the way in which

they are filled with electrons. In this regard, the band that contains the highest energy or valence electrons is termed the valence band, the conduction band is the next higher energy band, which is, under most circumstances, virtually unoccupied by electrons and is separated by an energy gap [Callister, 2007].

The difference in energy between the valence band (E_v) and the conduction band (E_c) is called an energy gap (E_g). This is the amount of energy that a valance electron must have in order to jump from the valence band to the conduction band, or is the energy required to break a bond to free an electron to conduction band and leave a hole in the valance band [SZE, 2002] .Once in the conduction band, the electron is free to move throughout the material and is not tied to any given atom [Floyd, 2002].

2.2.2 Conductor Energy Bands

This can be seen to be a result of their valence electrons being essentially free. In the band theory, this is depicted as an overlap of the valence band and the conduction band so that at least a fraction of the valence electrons can move through the material.

Metals are unique as good conductors of electricity. The most important fact about metals is that the valence band is not completely full of electrons, i.e. the valence band of metals contains empty states above and immediately adjacent to the Fermi level into which electrons can be excited.These states require only an infinitesimal energy excitation from the filled states at the Fermi level. Most of the thermal, electrical and optical properties of metals depend on this low excitation energy. In the band theory, this is depicted as an overlap of the valence band and the conduction band so that at least a fraction of the

valence electrons can move through the material. The energy band diagram for metals fall into two general classes:

For monovalent alkali metals such as sodium, the 3s energy band contains twice as many levels as there are Na atoms; however, only half of these levels are filled, Figure(2.5 a). For divalent alkaline earth metals such as magnesium the 3s and 3p energy bands overlap; this provides many empty states into which electrons can be easily excited.Figure (2.5 b) , [Callister, 2007].

2.2.3 Insulator Energy Bands

Most solid substances are insulators, and in terms of the band theory of solids this implies that there is a large forbidden gap between the energies of the valence electrons and the energy at which the electrons can move freely through the material (the conduction band) Figure (2.5 c).

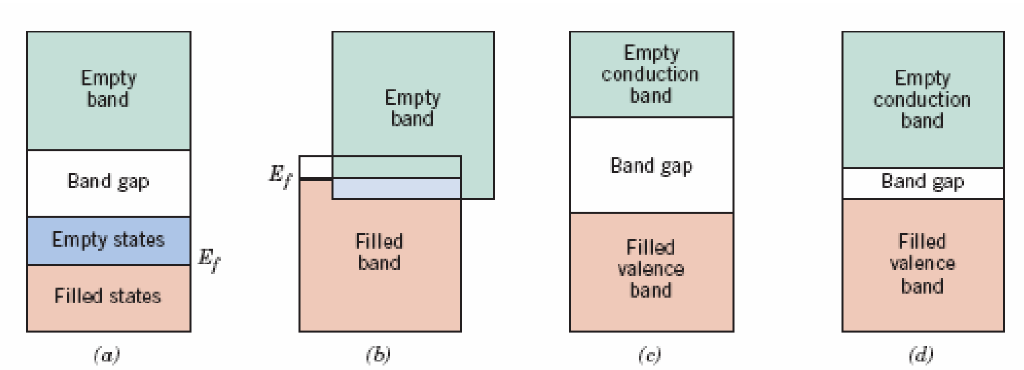


Figure (2.5): Energy band diagram of (a, b) a conductor with two possibilities, (c) an insulator and (d) a semiconductor. [Callister, 2007].

Glass is an insulating material which may be transparent to visible light for reasons closely correlated with its nature as an electrical insulator. The visible light photons do not

have enough quantum energy to bridge the band gap and get the electrons up to an available energy level in the conduction band. The visible properties of glass can also give some insight into the effects of "doping" on the properties of solids. A very small percentage of impurity atoms in the glass can give it color by providing specific available energy levels which absorb certain colors of visible light.

While the doping of insulators can dramatically change their optical properties, it is not enough to overcome the large band gap to make them good conductors of electricity. However, the doping of semiconductors has a much more dramatic effect on their electrical conductivity and is the basis for solid state electronics.

2.2.4 Semiconductor Energy Bands

For intrinsic semiconductors like silicon and germanium, the Fermi level is essentially halfway between the valence and conduction bands. Although no conduction occurs at 0 K, at higher temperatures a finite number of electrons can reach the conduction band and provide some current. If $E_g < 3\ k_BT$, for instance,electrons can jump thermally across the band gap and be promoted from the valence band to the conduction band. Both conduction band electrons and valence band holes charge carriers contribute then to the conduction.Figure(2.5 d)

The increase in conductivity with temperature can be modeled in terms of the Fermi function, which allows one to calculate the population of the conduction band. The valence band and conduction is separated by forbidden levels region called the energy gap.

In semiconductors and insulators, electrons are confined to a number of bands of energy, and forbidden from other regions. The conductivity of intrinsic semiconductors is

strongly dependent on the band gap, since electrons can gain enough energy to jump to the conduction band by absorbing either a phonon (heat) or a photon (light). The only available carriers for conduction are the electrons which have enough thermal energy to be excited across the band gap [Wikipedia website, 2011].

2.2.5 Dielectrics Materials

Understanding the structure of plastics (and in particular, the fluoropolymers) not only gives a better understanding of chemical resistance but also of the electrical properties.

Most plastics are dielectrics or insulators (poor conductors of electricity) and resist the flow of a current1. This is one of the most useful properties of plastics and makes much of our modern society possible through the use of plastics as wire coatings, switches and other electrical and electronic products. Despite this, dielectric breakdown can occur at sufficiently high voltages to give current transmission and possible mechanical damage to the plastic.

A dielectric material is one that is electrically insulating (nonmetallic) and exhibits or may be made to exhibit an electric dipole structure; that is, there is a separation of positive and negative charged entities on a molecular or atomic level. As a result of dipole interactions with electric fields, dielectric materials are utilized in capacitors [Callister, 1997].

When dielectric is placed in electric field, electric charges do not flow through the material, as in conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization, positive charges are displaced along the field and negative charges shift in the opposite direction. This creates an internal electric field which partly

compensates the external field inside the dielectric. The interaction of a dielectric with an electric field is conveniently described in terms of a parallel plate capacitor. Consider a parallel-plate capacitor that without a dielectric has a charge Q_0 and a capacitance C_0, Figure (2.6 a). The potential difference across the capacitor is $\Delta V_0 = Q_0 / C_0$. Hence, there is no path by which charge can flow and alter the charge on the capacitor. If a dielectric is inserted between the plates, Figure (2.6 b), the voltage between the plates decreases to a value ΔV and capacitance becomes (Serway, 2007):

$$C = \varepsilon' C_0 \qquad (2.13)$$

That is, the capacitance increases by a factor ε' when the dielectric completely fills the region between the plates. For a parallel-plate capacitor, where $C_0 = \varepsilon_0 A / d$ then the capacitance when the capacitor is filled with a dielectric will be:

$$C = \varepsilon' \varepsilon_0 A / d \qquad (2.14)$$

where ε' is a dimensionless factor called the relative dielectric constant or relative permittivity of the material and it is the property of the material related to its atomic structure. A is the area of parallel plates and d is the distance of separation between them.

The ratio of the dielectric constant of the material ε to the vacuum dielectric constant (permittivity of free space, ε_0) is called the relative dielectric constant or simply dielectric constant [Jastrzebski, 1977]:

$$\varepsilon' = \varepsilon / \varepsilon_0 \qquad (2.15)$$

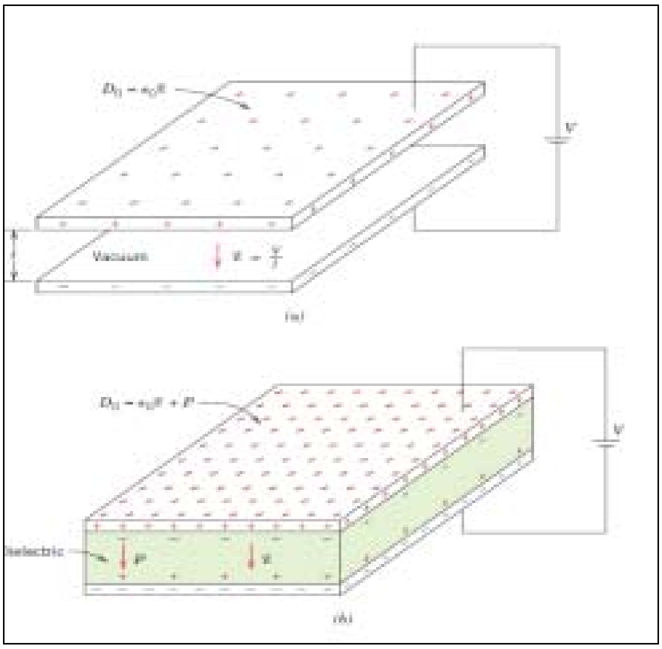


Figure (2.6): A parallel-plate capacitor (*a*) when vacuum is present and (*b*) when a dielectric material is present [Callister, 2007].

The dielectric constant is a measure of the influence of a particular dielectric on the capacitance of a condenser. It measures how well a material separates the plates in a capacitor and is defined as the ratio of the capacitance of a set of electrodes with the dielectric material between them to the capacitance of the same electrodes with a vacuum between them. The dielectric constant for a vacuum is 1 and for all other materials it is greater than 1, in **SI** units, $\varepsilon_0 = 8.854*10^{-12}$ farad per meter. (http://www.zeusinc.com)

2.2.6 Polarization

The application of an electric field to a dielectric material produces a displacement of the charge within the material through a progressive orientation of permanent or induced dipoles. This phenomenon is known as dielectric polarization. The electric dipoles orient

themselves between the two charged plates (electrodes) in such a way that the negative charges tend to move toward positive electrode, whereas the positive charges tend to move toward negative electrode. Since the charges are not free to move, they don't flow, and the interior body doesn't become an equipotential region. A quantitative measure of the displacement charge effect of the material is the dielectric constant, which has a characteristic value for each material [Jastrzebski, 1977].

- Types of polarization

Polarization is the alignment of permanent or induced atomic or molecular dipole moments with an external applied electric field. Dielectric materials ordinarily exhibit at least one of these polarization types, There are three types or sources of polarization depending on the dielectric material and also the manner of the external field application.

- Electronic Polarization

It arises because of a minute displacement of the positive nucleus and the negative electronic cloud in opposite directions under the action of an electric field figure (2.7).

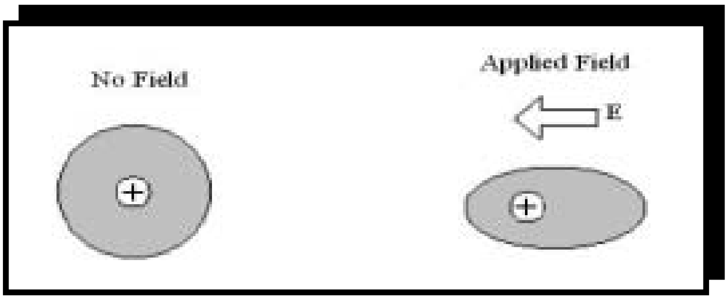


Figure (2.7): Electronic polarization. [Anderson, 1964].

This type of polarization occurs in all atoms, and can be observed in all dielectrics irrespective of whatever other types of polarization are displayed in the dielectric. This process can be established in a very short time (~10^{-15}s), and approximately corresponds to the frequency of the ultraviolet radiation (f >>10^{14} Hz). [Anderson, 1964]

- Ionic Polarization

When an external electric field is applied to an ionic material, the cations will be displaced in the field direction and the anions will be displaced against, an

induced dipole moment formed in a time interval of about (10^{-13} – 10^{-12} s); this time corresponds to the frequency of infrared radiation figure(2.8). [Tarreev, 1979].

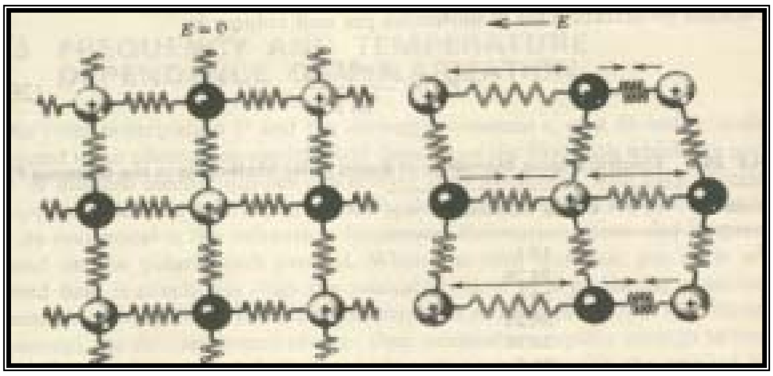


Figure (2.8): Ionic polarization. [Ralls, 1976].

In summary, the process of the electronic and ionic polarization may be regarded as varieties of polarization caused by deformation, which is displacement of charges with respect to each other in the presence of electric field; because of this deformation, the process is called distortional polarization [Anderson, 1964].

- **Orientational Polarization**

Orientational or dipolar polarization arises in substance built up of polar molecules possessing a permanent electric dipole moment. Under an applied electric field the polar molecules tend to rotate and orient themselves in the direction of the electric field figure (2.9). This tendency towards alignment is opposed by the thermal agitation of the molecules. Increasing of temperatures lead to a greater tendency toward randomness, then smaller degree of orientation. Thus orientational polarization is strongly temperature dependent in contrast to the induced polarization, which is practically independent of temperature. Orientational polarization occurs mainly in gases and liquids where molecules are fairly free to rotate. In some solids, the rotation of polar molecules may be restricted by the lattice forces, which may greatly reduce the orientation polarization effect [Tarreev, 1979].

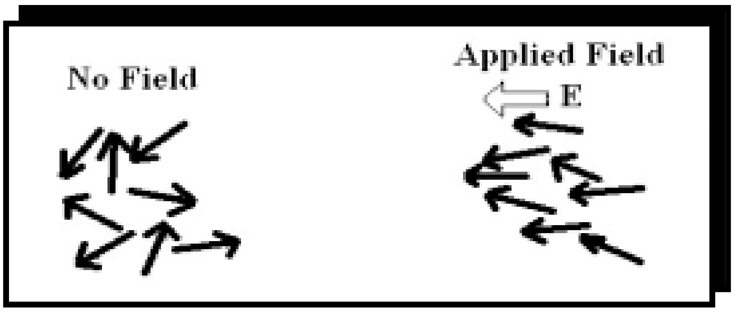


Figure (2.9): Orientation polarization. [Tarreev, 1979].

The basic electronic and atomic polarization leads to a general classification of dielectrics, which all fall into one of three groups:

(a) Non- polar materials, which show variations of permittivity in the optical range of frequencies only, this includes all those dielectrics having a single type of atom, whether they are solids, liquids, or gases.

(b) Polar materials having variation of permittivity in the infrared as well as the optical region: the most important members of this group are the ionic solids, such as rock salt and alkali halide crystals, in general.

(c) Dipolar materials that also show orientational polarization, this embraces all materials having dipolar molecules of which one important common one is water. The chemical groups O-H and C=O are dipolar and may impart dipolar properties to any material in which they occur [Anderson et. al., 2003].

2.2.7 The Frequency Dependence of the Polarization.

The Dielectric constant ε' of the dielectric material subjected to an alternating field depends on the ease with which the permanent or induced electric dipoles can reverse their alignment with each reversal of the applied field. The time required for dipole reversal is called the relaxation time. Relaxation times and frequencies depend on the polarization process. At low frequencies, the dipoles have sufficient time to orient themselves completely along the instantaneous direction of the field. If the field frequency is much greater than the relaxation frequency (or much less than the relaxation time), the dipoles cannot change their orientation rapidly enough to remain oriented with the applied field. Thus, the particular polarization process will not contribute to the total polarization [Rails, 1976].

Because both electronic and ionic polarization involve repositioning of charges over lattice dimensions less than the atomic diameter, these types of polarization persist to high frequencies, that is, up to the ultraviolet frequency range for electronic polarization and up to the infrared frequency range for ionic polarization. By contrast, molecular orientation

polarization only persists to frequencies in the microwave frequency range since it involves reorientation on a molecular scale. As shown in figure (2.10). Thus, we can define the relaxation time as the average time necessary to change from the original state to the final state or the average length of time that is required for a system to move toward its equilibrium state. This time is much shorter in atomic polarization and still much less in electronic polarization, as in Figure (2.10). Thus, at a frequency as high as the optical frequency range, only electronic polarization contributes to the dielectric constant [Jastrzebski,1977].

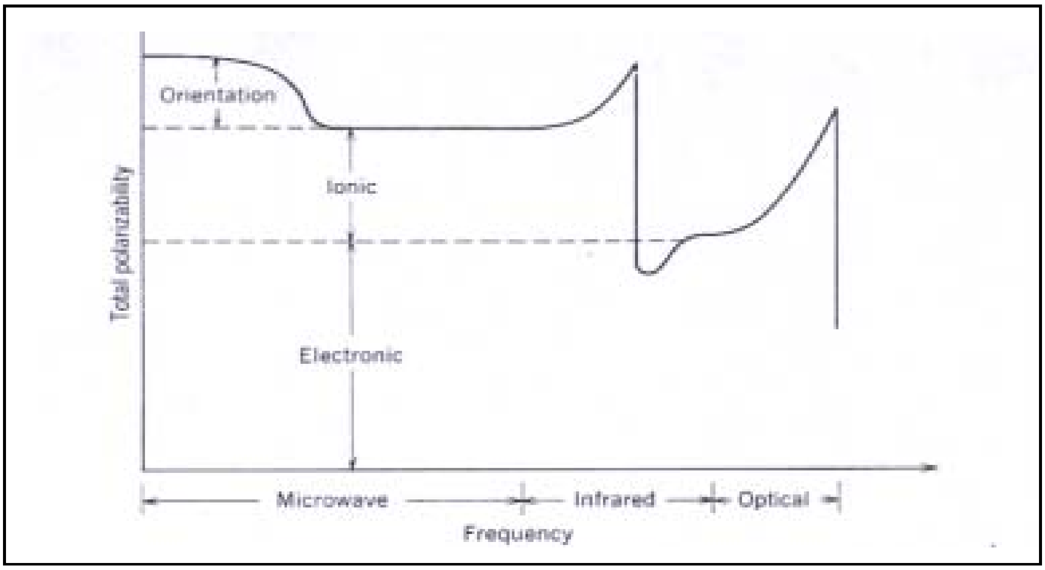


Figure (2.10): Frequency effect on polarization [Jastrzebski, 1977].

2.2.8 Temperature dependence of polarization

The temperature dependence of polarization is strongly related to the molecular, ionic, or atomic arrangements in a substance as well as the dominant polarization mechanism. In many ionic solids and some having both covalent and ionic natures, polarization increases with temperature, provided that the frequency of the applied field is **not** too high. This effect is due to the increased ionic mobilities at higher temperatures, which effectively reduce the relaxation time. Nitrobenzene, for example, is a large molecule with a permanent dipole moment that should lead to a large orientation polarization. At low temperatures molecular motion is hindered by the molecules themselves; and permanent dipoles can't reorient themselves in an alternating field. Thus the relaxation time for orientation polarization is very large. At higher temperatures (closer to melting point), the individual molecules become much more mobile and the relaxation time decreases, so the orientation polarization dominates [Ralls, 1978].

2.2.9 Dielectric Losses (ε'')

Dielectric losses result from the heating effect on the dielectric material between the conductors. The heat produced is dissipated into the surrounding medium. Under an applied electric field, energy in the form of an electric charge is stored by the dielectric material. Many of these charge carriers are naturally polarized dipoles, and realign themselves by rotation in the direction of the applied field.

The orientation of the dipoles and the resultant rotation is opposed by the internal friction of the material and the thermal agitation of the molecules. Energy required

maintaining this rotation accounts for power loss. These losses depend on the frequency of the applied field but, at very high frequencies, the losses may be smaller because the field reverses so rapidly that the dipoles never become aligned completely with the field. Dielectric losses of an insulating material may be caused by the absorption of electrical energy (internal dipole friction) and by leakage currents through the material. Leakage occurs by condition, which appears mainly ionic in nature and is usually negligible except at high temperatures. The absorption losses under an alternating electric field result in dissipation of the electric energy as heat in the material. An ideal dielectric does not absorb electrical energy, and the charge of a capacitor is completely recovered on the removal of the electric field. A real dielectric material, however, always causes some loss of electrical energy although, in many cases, it is very small. This loss is measured by a phase difference between the phase angle and the 90° angle of an ideal capacitor. Energy losses are important in high-frequency designs, not only because they represent a lack of efficiency, but also because energy losses change the impedance of the circuit [Harlow, 2004].

Loss factor is the product of the dissipation factor and dielectric constant, and it is a measure of the actual power loss in the insulation. The dissipation factor is the fraction of the energy lost during a cycle. The loss factor is affected by the frequency of the electric field. As it had mentioned above, at low frequencies the dipoles have sufficient time to orient themselves completely along the instantaneous direction of the field. This orientation occurs first in one direction and then in the other, following the change in direction of the field. The resulting dipole rotation is opposed by internal friction of the material and the thermal agitation of the molecules [Jastrzebski, 1977].

All dielectrics (except vacuum) have two types of losses. One is a conduction loss, representing the flow of actual charge through the dielectric. The other is a dielectric loss due to movement or rotation of the atoms or molecules in an alternating electric field. Dielectric losses in water are the reason for food and drink getting hot in a microwave oven. One way of describing dielectric losses is to consider the permittivity as a complex number, defined as

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = |\varepsilon|\, e^{-i\delta} \qquad \text{……………………} \quad (2.16)$$

where

ε' = dielectric constant

ε'' = dielectric loss factor

δ = dielectric loss angle

Equation (2. 16) expresses the complex permittivity (ε^*) in two ways, as real (ε') and imaginary (ε'') or as magnitude and phase. The magnitude and phase notation are rarely used. Instead, people usually expressed the complex permittivity by ε' and tan δ is called either the loss tangent or the dissipation factor .

2.2.10 Resistors and capacitors in AC- Circuits

When a time varying potential is applied across a material a sinusoidal current flows as a consequence. The equivalent resistor for all elements in the electrical circuit (such as resistors, capacitors and inductors) is called impedance.

This section will be concerned with the description of alternating current (ac) circuits. In the beginning an investigation of the characteristics of simple circuits that contain resistors

and capacitors will be produced. Then the analysis of the parallel RC connection in these circuits will be discussed [Serway, 2007].

2.2.11 Resistors

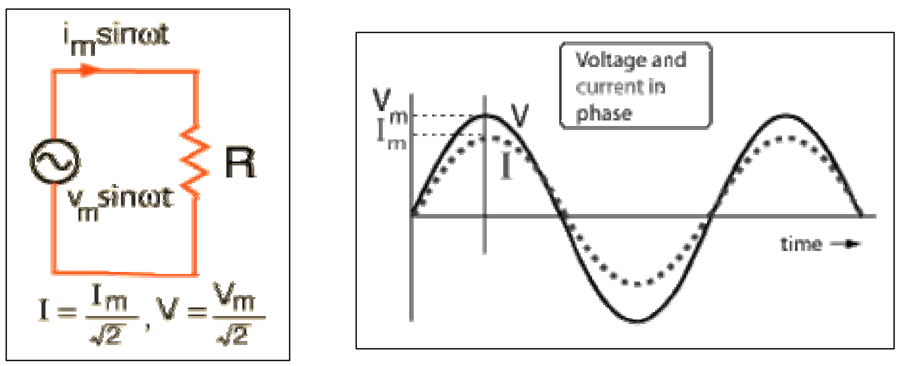
Let us consider the pure resistance shown in Figure (2.11a) connected to an ac generator. At any particular instant, Ohm's law applied to the resistor tells us that V = I R. The ac voltage is given by:

$$V = V_{max} \sin \omega t \tag{2.17}$$

,where V is the instantaneous voltage drop across the resistor. Therefore the instantaneous current in the resistor is:

$$I = V / R = (V_{max} / R) \sin \omega t = I_{max} \sin \omega t \tag{2.18}$$

, where I_{max} is the maximum current and it is given by ($I_{max} = V_{max} / R$).



(a) (b)

Figure (2.11): A diagram of (a) a pure resistance in an ac circuit and (b) plot of V versus I across the resistor as a function of time [Hyper physics website].

From equations (2.17) and (2.18), we can see that the instantaneous voltage drop across the resistor is [Serway, 2000]

$$V = I_{max} R \sin \omega t \qquad (2.19)$$

Because current and voltage both vary as (sin ω t) and reach their maximum values at the same time in pure resistance ac circuit, they are said to be in phase see Figure (2.11b).

2.2.12 Capacitors

For a capacitor in an ac circuit as in Figure (2.12a) connected across the terminals of an ac generator, the instantaneous voltage drop across the capacitor is given by [Serway, 2007]:

$$V = V_{max} \sin \omega t \qquad (2.20)$$

From the definition of the capacitance Equation (2.15), we get that $Q = C$ V. Substituting the value of V given in Equation (2.20), gives:

$$Q = C V_{max} \sin \omega t \qquad (2.21)$$

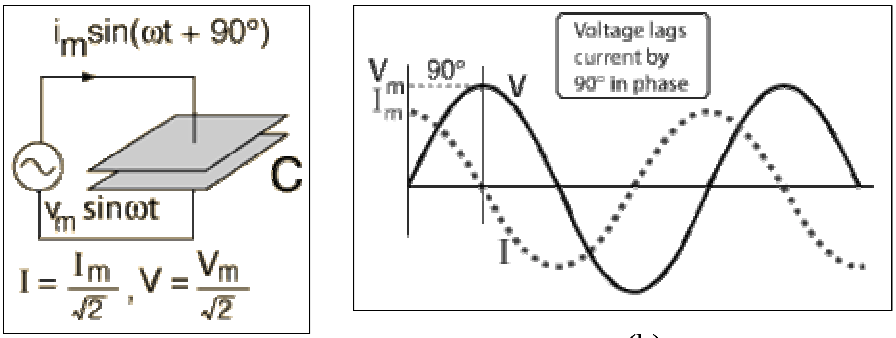
Since I = dQ / dt, differentiating this equation gives the instantaneous current in the circuit:

$$I = d Q / d t = \omega C V_{max} \cos \omega t \qquad (2.22)$$

Here we can see that the current is not in phase Figure (2.12b) with the voltage drop across the capacitor, given in Equation (2.18). Using the trigonometric identity [cos ω t = sin (ω t + π /2)] in last equation we get:

$$I = C (d V / d t) = (1 / \chi_C) V_{max} \sin (\omega t + \pi /2) \qquad (2.23)$$

, where χ_C is the capacitor reactance; χ_C = (ω *C*)$^{-1}$. Comparing Equation (2.23) with Equation (2.20), we can see that there is a phase difference (*φ*) between the current and voltage across the capacitor (*φ* = π /2 radian = 90°) as shown in the figure, [Serway, 2007].



(a) (b)

Figure (2.12): A diagram of (a) a capacitor in an ac circuit and (b) plot of V versus I as a function of time across the capacitor [Hyper physics website].

2.2.13 Parallel connection of R & C

In the RC circuit shown in Figure (2.13), a capacitor C is connected in parallel with resistor R, the total current is given by:

$$I = I_R + I_C \qquad (2.24)$$

Substituting Equations (2.18) and (2.23) in this equation we have:

$$I = \frac{V_{\max}}{R}\sin\omega t + \frac{V_{\max}}{\chi_C}\sin(\omega t + \frac{\pi}{2}) \qquad (2.25)$$

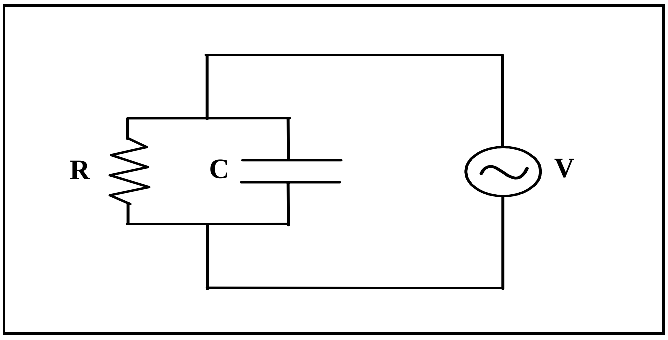


Figure (2.13): Parallel connection of R & C in an ac circuit [Hyper physics, 2005]

The equivalent Ohm's law for the RC parallel circuit in Figure (2.13) is given by:

$$V = Z\,I \qquad (2.26)$$

, where Z is called the impedance of the circuit. From Equation (2.25) we can see that:

$$\frac{1}{Z} = \frac{1}{R} + i\omega\, C \qquad (2.27)$$

$$Z = \frac{R}{1 + i\omega\, C\, R} \qquad (2.28)$$

, since: Z = Z' – *i* Z''. We can separate the real component of the impedance Z' and the imaginary component of the impedance Z'' via multiplication by (1 – *i* ω *C* R), the complex conjugate. Thus:

$$Z = \frac{R\,(1 - i\omega\, C\, R)}{1 + (\omega\, C\, R)^2} \qquad (2.29)$$

$$Z' = \frac{R}{1 + (\omega\, C\, R)^2} \qquad (2.30)$$

$$Z'' = \frac{\omega\, CR^{\,2}}{1 + (\omega\, CR\,)^2} \qquad (2.31)$$

If we apply AC voltage across a capacitor filled with a dielectric material, the complex form of the voltage is:

$$V = V_{max}\, e^{-i\,\omega\, t} \qquad (2.32)$$

The charge in the capacitor at time (t) can be written as: $Q = C^{*}$ V, where C^{*} is the complex capacitance that given by:

$$C^{*} = \varepsilon^{*} C_0 \qquad (2.33)$$

, where ε^{*} is the complex permittivity and C_0 is the geometrical capacitance which is given in Equation (2.12). The current is given by:

$$I = dQ / dt = i\, \omega\, C^{*}\, V \qquad (2.34)$$

Using Equation (2.33), we will get:

$$I = i\, \omega\, \varepsilon^{*} C_0\, V \qquad (2.35)$$

Dividing by (V), then the impedance equation writes

$$I / V = 1 / Z = i\, \omega\, C_0\, \varepsilon^{*} \qquad (2.36)$$

Comparing this equation with Equation (2.27), we will get the following formula for the parallel RC circuit;

$$i\, \omega\, C_0\, \varepsilon^{*} = (1 / R) + i\, \omega\, C \qquad (2.37)$$

By using this equation, knowing that ($\varepsilon^{*} = \varepsilon' - i\, \varepsilon''$), we directly get that:

$$\varepsilon' = C / C_0 \qquad (2.38)$$

$$\varepsilon'' = 1 / \omega\, C_0\, R \qquad (2.39)$$

, where ε' is the real part of the complex relative permittivity and called the (dielectric constant), and ε'' is the imaginary part of the complex relative permittivity and called the (dielectric loss). Consequently the loss tangent can be given by [Tareev, 1979]:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{1}{\omega\, C\, R} \qquad (2.40)$$

2.2.14 Analysis Equations

The complex impedance of the sample with the real and imaginary components can be calculated by:

$$Z' = Z \cos \varphi \tag{2.41}$$

$$Z'' = Z \sin \varphi \tag{2.42}$$

The dielectric constant ε' and the dielectric loss ε'' of the sample are calculated from the following equations (Elimat, 2008):

$$\varepsilon' = \frac{Z''}{2\pi f C_o Z^2} \tag{2.43}$$

$$\varepsilon'' = \frac{Z'}{2\pi f C_o Z^2} \tag{2.44}$$

where f is the frequency of the applied AC electric field and C_0 is the capacitance of the two plates of the cell (capacitor) without the sample (dielectric), and it was given in Equation (2.12).

Hence, a plot of Z' and Z'' (or ε' and ε'') yields a semicircle in the complex impedance diagram. The maximum value of Z' (or ε'') is obtained when $\omega_{max}\, \tau = 1$, which corresponds to the frequency: $\omega_{max} = 1/\tau$ (where: $\omega_{max} = 2\pi\, f_{max}$). This equation enables the relaxation time to be calculated in a simple manner from experimental data. The graph of ε'' versus ε' in the complex plane is an implicit function of frequency (a so-called Cole-Cole plot) is shown in Figure (2.14) [Elliot, 2000].

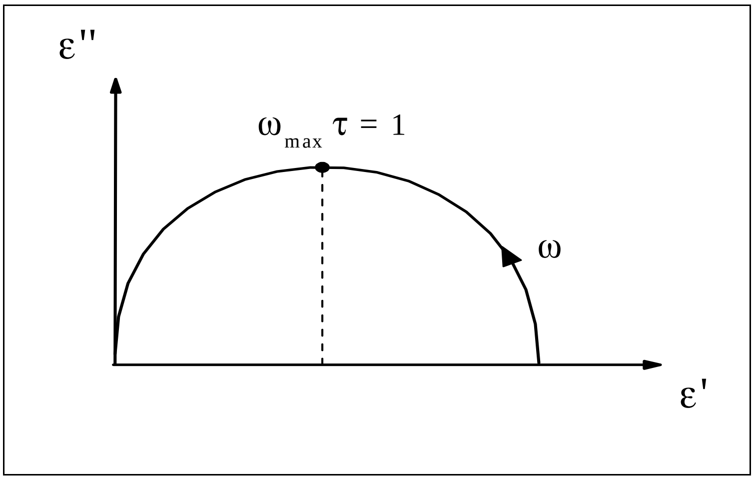


Figure (2.14): The Cole-Cole plot of ε'' versus ε' [Elliot, 2000].

The AC conductivity of the sample calculated from the following equation

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'' \qquad (2.45)$$

The activation energy (E_a) of the conduction process is calculated by Arrhenius equation, which is given by [Jastrzebski, 1977]:

$$\sigma = \sigma_0 \exp [- E_a / k_B T] \qquad (2.46)$$

where σ is the electrical conductivity, σ_0 is the material constant conductivity, T is the temperature of the material in Kelvin, and k_B is the Boltzmann constant($k_B = 1.38 \times 10^{-23}$ Joule / K) [Hummel, 1993].

2.3 Thermal properties

Thermal properties are the response of a material to the application of heat. As a solid absorbs energy in the form of heat, its temperature rises and its dimensions increase. The energy may be transported to cooler regions of the specimen if temperature gradients exist, and ultimately, the specimen may melt.

Heat is transported in solid materials by both lattice vibration waves (phonons) and free electrons. A thermal conductivity is associated with each of these mechanisms, and the total conductivity is the sum of the two contributions, or

$$K = k_l + k_e \qquad (2.47)$$

Where k_l and k_e represent the lattice vibration and electron thermal conductivities, respectively; usually one or the other predominates. The thermal energy associated with phonons or lattice waves is transported in the direction of their motion. The k_l contribution results from a net movement of phonons from high- to low temperature regions of a body across which a temperature gradient exists.

Free or conducting electrons participate in electronic thermal conduction. Free electrons in a hot region of the specimen is imparted a gain in kinetic energy. They then migrate to colder areas, where some of t kinetic energy is transferred to the atoms themselves (as vibrational energy) as a consequence of collisions with phonons or other imperfections in the crystal. The relative contribution of k_e to the total thermal conductivity increases with increasing free electron concentrations, since more electrons are available to participate in this heat transfer. (Callister, 2007).

2.3.1 Thermal Properties of Solid Materials

Heat conduction in solids is mediated mainly by the elastic waves or phonons only as the result of the molecular vibration of the lattice, where there are no free electrons. Thermal conductivity of polymers can be described by Debye and Eiermann model (Kittel, 2007) as:

$$k = \frac{1}{3} c_\upsilon \rho \upsilon \lambda \qquad (2.48)$$

Where, C_v is the heat capacity of phonons per unit volume, ρ is the volume density, υ is the propagation speed of the phonons through the lattice and λ is the mean free path between collisions determined by two successive processes: geometrical scattering and scattering by other photons.

2.3.2 Dependence of Thermal Conductivity on Temperature

The temperature dependence of the thermal conductivity of polymers depends mainly on the polymer structure [Elimat and Zihlif, 2006]. For amorphous polymers the thermal conductivity will increase with increasing temperature [Nyilas, 1996], while in case of crystalline polymers the thermal conductivity decreases as temperature increases [Kubicar, 1991]. The thermal conductivity of solid semi-crystalline polymers decreases as density decreases and temperature increases. The decrease in density is a consequence of a decrease in crystallinity [Katsure and Kamal, 1987].

2.3.3 Factors Affecting the Thermal Conductivity

Generally, the thermal conductivity of polymer composites is influenced by some factors:

1) Chemical constituents, structure, type of defects.

2) Physical nature and material phase (solid or melt).

3) Molecular weight (thermal conductivity increases with increasing the molecular weight).

4) Structural changes as crystallinity and morphology.

5) Bond strength and molecular motion in chains.

6) The anisotropy in bonding forces.

7) The chain orientation (preferred anisotropy).

8) Degree of polymerization.

9) Phase transitions.

10) Conditions of polymer processing and preparation environment.

11) The type and nature of the filler.

12) The boundary conditions of the experiment.

13) The geometry of the test sample.

2.3.4 Thermal conductivity measurements

Thermal conductivity represents the amount of heat energy conducted per unit time through a unit area (perpendicular to the direction of heat transfer) when the temperature gradient across the heat-conducting element is one unit. Conduction of heat in insulating solids can be due to thermally excited lattice vibrations (phonons), thus the thermal conductivity is caused by phonon transport as a major contributor and a result of existing some electrons and metallic impurities. [EI-Rahman et al, 1996].

The thermal conductivity (k) is given by the familiar relation:

$$H = \frac{dq}{dt} = -Ak\frac{dT}{dL} \qquad (2.49)$$

Where $\frac{dq}{dt}$ is the time rate of heat flow transport as a result of the temperature gradient $\frac{dT}{dL}$, and *A* is the sample cross-section area as in Fig. (2.15).

Under steady-state condition the sample temperature becomes constant, the temperature gradient is the temperature difference between the specimen faces, and ΔL is the specimen thickness and the rate heat flow becomes [Tabor, 1995]:

$$\frac{\Delta q}{\Delta t} = -Ak\left(\frac{\Delta T}{\Delta L}\right) \tag{2.50}$$

where $\Delta T = T_2 - T_1$ is the temperature difference between the specimen faces, and ΔL is the specimen thickness.

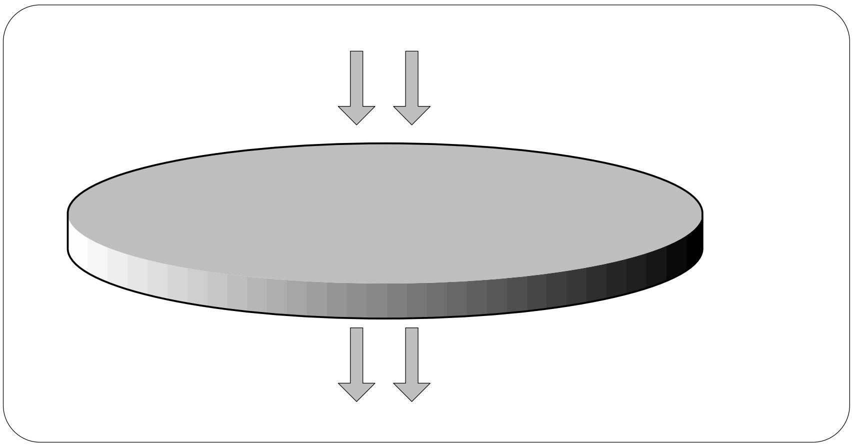


Figure (2.15): Heat flow across a solid disk of cross section area A

The quasi-state temperature difference ΔTs were found to be identical for the thermocouple pairs on one side, and those on the other sides. This gives support to the

assumption of symmetry on both sides of the heat flux. The values of thermal conductivity (k), at each temperature can be calculated from the relation:

$$k = q_s\left(\frac{L}{\Delta T_s}\right) = \frac{IVL}{2A\Delta T_s} \quad (\mathrm{W/m.^0C}) \qquad (2.51)$$

where q_s are the heat flux, *I* the electrical current, *V* the electrical voltage, and *A* the area of the heating foil. The factor 2 is due to the symmetrical distribution of heat flux on both sides of the apparatus [Katsure and Kamal, 1987]. This is because we used two circular disks of identical thickness.

2.3.5 Thermal Parameters Relations

Some thermal quantities are related to thermal conductivity (*k*) as:

i. The thermal resistivity (*r*) is the reciprocal of the thermal conductivity

$$r = \frac{1}{k} \quad (m.^oC/W) \qquad (2.52)$$

ii. The thermal resistance (R) is given by the equation:

$$R = \frac{L}{k} \quad (m^2.\ ^oC/W) \qquad (2.53)$$

iii. The Lorenz number of a solid defined as the ratio of thermal and electrical conductivity is inversely proportional to the absolute temperature in the form of the equation:

$$L = (k/\sigma T)\ (W.\Omega/K^2) \qquad (2.54)$$

Where σ is the DC electrical conductivity, k is the thermal conductivity (Kumar and Prasad, 1993).

CHAPTER THREE
EXPERIMENTAL WORK

The material investigated in this study is PEO/NaI electrolyte composites with different NaI (filler) concentrations (1 wt. %, 2 wt. %, 4 wt. %, 6 wt. %, 8 wt. %, 10 wt. %, 15 wt. %) and neat PEO sample for comparison.

3.1 Materials and Composites Films Preparation

Poly (ethylene oxide) with average molecular weight of 300,000 g/mol was used to prepare composite films of PEO/ NaI by casting from solution made of PEO and sodium iodide (NaI). Poly (ethylene oxide) powder and NaI powder were mixed together and dissolved in methanol as a suitable solvent. The solution was then stirred continuously by a rotary magnet at room temperature for few days until the mixture appear in a homogeneous viscous molten appearance. The mixture was immediately casted to thin films on to a glass mould (plate) and the methanol allowed to evaporate completely at room temperature by waiting for a few days under atmospheric pressure. All the samples were dried in the oven at 40ºC for two days. This procedure provided thin films of 70 µm thick films.

3.2 Optical Measurements

The most direct and perhaps the simplest method for probing the band structure of materials is to measure their absorption spectrum. Using the ultraviolet (UV) visible spectrophotometer, located in the Chemistry Department at Jordan University Figure (3.1), the optical absorbance and reflectance spectra of the PEO/NaI composites were collected at room temperature in the wavelength range of 300 – 800 nm. The absorption coefficient

$\alpha(\omega)$ was calculated from the absorbance *A*, after correction for reflection, *α (ω)* was calculated using the relation:

$$I = I_0 \exp(-\alpha x) \qquad (3.1)$$

Hence,
$$\alpha(w) = \frac{2.303}{x} \log\left(\frac{Io}{I}\right) = \frac{2.303}{x} A(\omega) \qquad (3.2)$$

where x is the sample thickness (x= 0. 007 cm), I_0 and I are the incident and transmitted intensities, respectively.

On the other hand, *α (ω)* is related to the optical transmittance (*T*) and reflectance (*R*) as follows

$$\alpha(\omega) = \frac{1}{x} \log\left\{ \frac{(1-R)^2}{2T} + \frac{(1-R)^2}{\sqrt{(2T)^2 + R^2}} \right\} \qquad (3.3)$$

and the refractive index can be obtained from

$$n = \left\{ \left[\frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{R+1}{R-1} \right\} \qquad (3.4)$$

where *k* is the extinction coefficient which is related to the absorption coefficient and the wavelength,(Al-Ramadin,2000) by

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3.5)$$

The dielectric constant (ε') and dielectric loss (ε'') is calculated from the relations:

$$\varepsilon' = n^2 - k^2$$

$$\varepsilon'' = 2nk \qquad (3.6)$$



Figure (3.1): Cary Spectrophotometer

3.3 Impedance Measurements

The study of the effect of filler concentration and frequency of the applied electric field on impedance, phase angle, tan loss, real and imaginary part of impedance, AC-conductivity of PEO and PEO/ NaI composites were carried out using the following devices:

1) **Impedance Analyzer:**

Here we used the Hewlett Packard (HP) 4192A impedance analyzer which gives the impedance and phase angle by varying the applied frequency (ranges from 5Hz up to 13MHz), which is shown in Figure (3.2). The specimen was placed firmly between two copper electrodes in a sample holder shown in Figure (3.3). These electrodes are connected through cables to the impedance analyzer. Impedance measurements have been performed in a frequency range from about 30 kHz up to 5 MHz over a range of temperature (27ºC - 60 ºC) with steps of 10ºC. Since the melting temperature (T_m) for PEO is about 66 ºC, no higher temperature measurements were conducted.

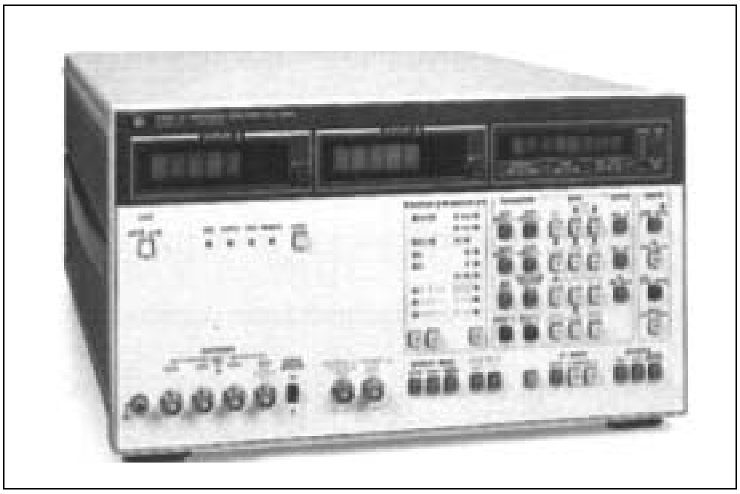


Figure (3.2): Hewlett Packard 4192A impedance analyze

2) **Oven Chamber:**

In order to study the effect of temperature on the impedance and phase angle, the sample holder with the test specimen were inserted inside an oven chamber. Accurate temperature readings were taken by a thermocouple in addition to the temperature readings of the oven dial after a steady state is reached. The accuracy of temperature readings is ± 1 ^{o}C. Impedance measurements have been performed in a temperature range from 27 °C up to 60 °C with steps of 10°C, below the melting temperature ($T_m \approx -65$ °C) of PEO polymer.

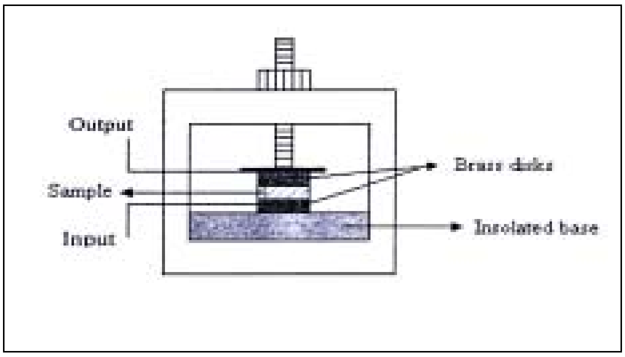


Figure (3.3): The sample holder diagram

The values of impedance (Z) in ohm's (Ω) and the phase angle (φ in degrees) were measured directly using Hawllet-Packard 4192A impedance analyzer. Following data acquisition, the required calculations were carried out using the analysis equations discussed in the previous chapter. We have calculated the dielectric constant, AC conductivity and other values of PEO/NaI composites. The calculations and graphical representations were done using computer and special software programs.

3.4 Thermal Conductivity Measurements

The procedure of thermal conductivity measurements relies on:

1) Apparatus

Measurements of thermal conductivity were carried out at the laboratory of "physics of materials" at the Physics Department in Jordan University using the measuring components shown in Figure (3.4).

1. Thermocouple Amplifier (model A D 594 instrumentation amplifier); calibrated as (10 mV/°C), Figure (3.5).
2. Sample holder, Figure (3.6) which contains:
    a) Two small disk samples (5 cm in diameter and 3 mm thickness), each is sandwiched between two plate.
    b) Heater: sandwiched between two insulators. The heater used is made of chrome and has a power of 100 watt.
    c) Two sheets of teflon used as insulators.

d) Five thermocouples, each of the samples is in contact with two thermocouples, and the fifth thermocouple is for the whole system, Figure (3.7).

e) Teflon tapes.

f) Aluminum plates.

3. The Oven

4. Power supply.

5. Multimeters.

6. Stop watch.

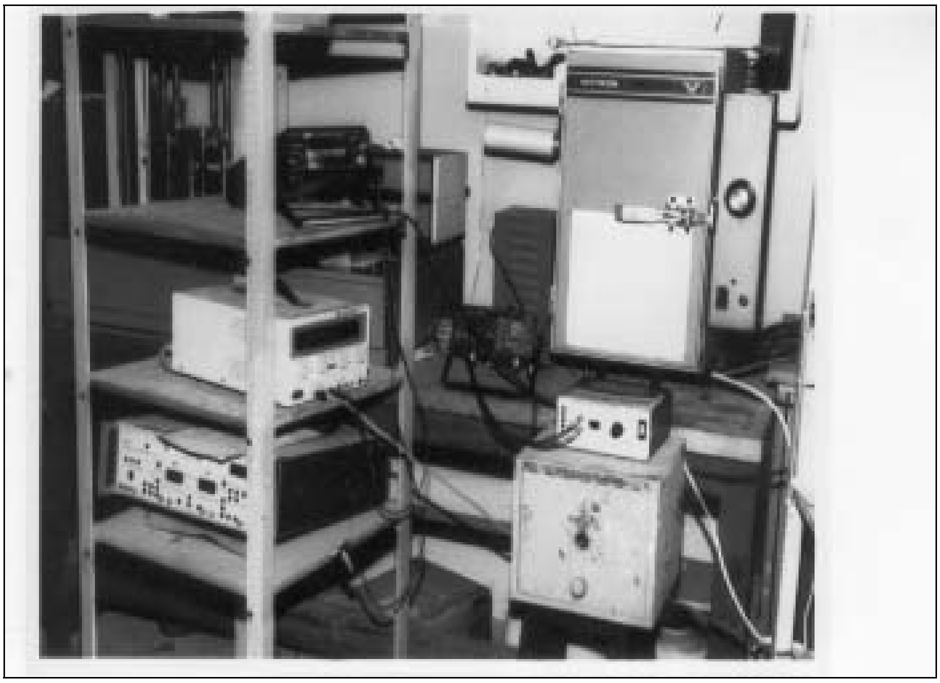
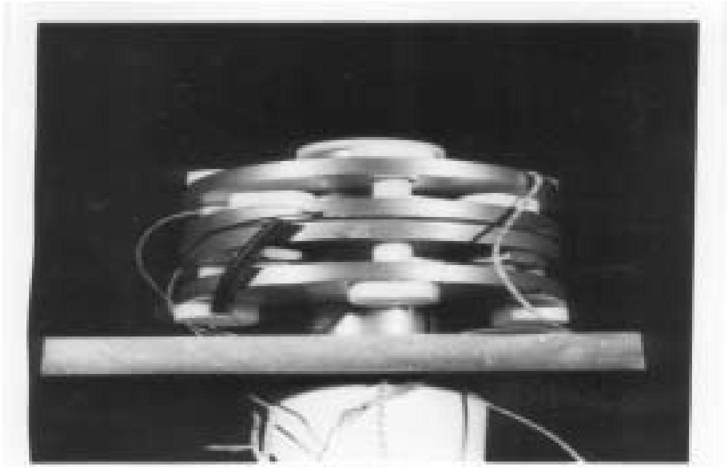


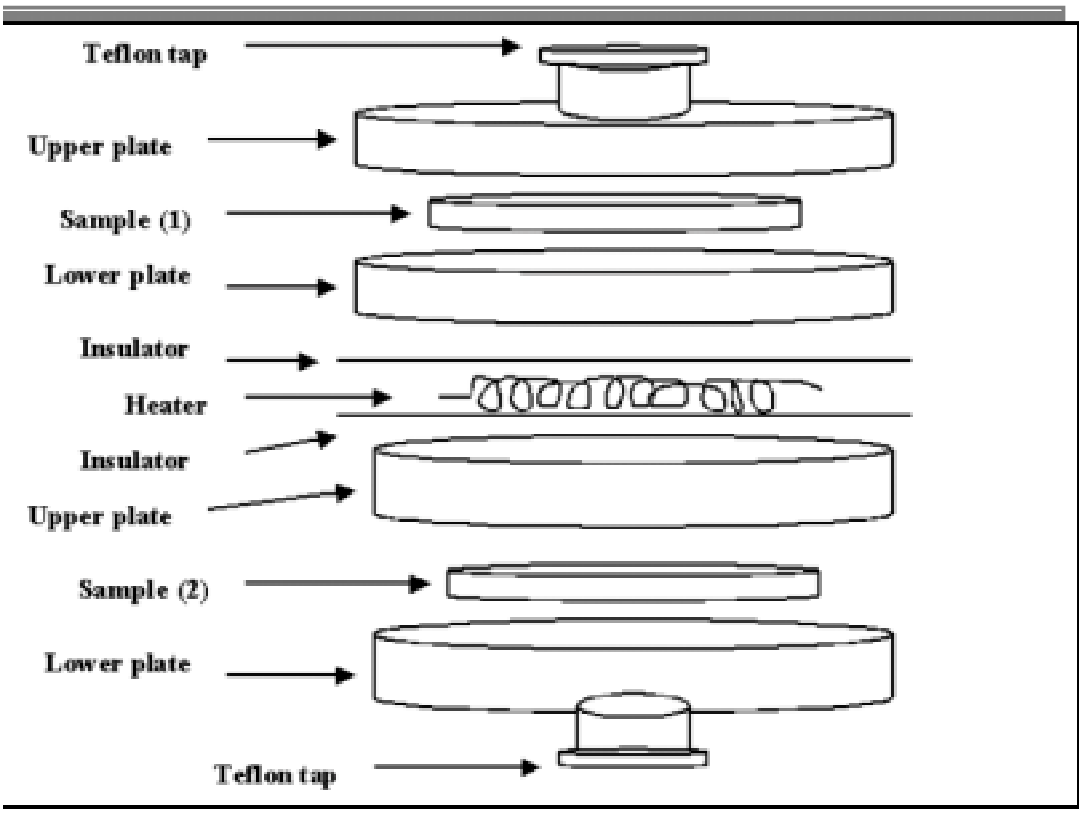
Figure (3.4): The setup used in thermal conductivity measurements



Figure (3.5): Thermocouple amplifier (AD594 instrumentation)



(a)



(b)

Figure (3.6): a) a photo of the used sample holder and b) a schematic diagram of the used sample holder.

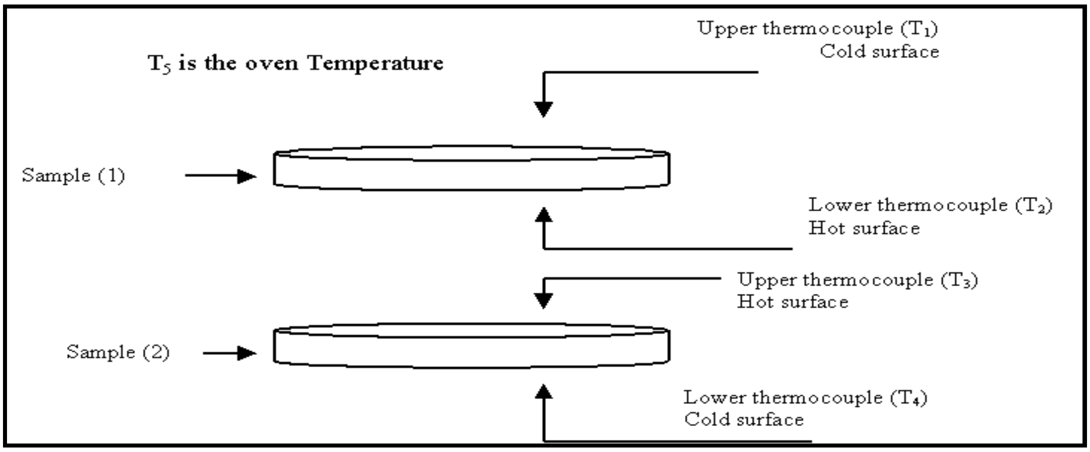


Figure: (3.7): set up of the used thermocouples in the sample holder

2) Procedure of thermal conductivity measurements.

1) Preparing two disks of the composite samples, putting them in the sample holder placed in the oven.

2) Connect the apparatus in a circuit as illustrated in Fig. (3.4).

3) The apparatus measures the thermal conductivity using the steady state method, where the hot and cold plates are maintained at constant temperature, measured by thermocouples fixed on the sample surfaces.

4) Giving the pulse voltage (V) for 30 seconds, just arriving to the steady state, recording the current (I) value.

5) Arriving the second constant state, to indicate (ΔT) between the hot and the cold plates for each sample.

6) The thermal conductivity in (W/ m.^{o} C) was calculated using the relation:

$$k = IV\frac{L}{2A\Delta T} \tag{3.7}$$

Where: *I*: is the pulse current (Ampere).

V: is the pulse voltage (Volt).

L: is the sample thickness (m).

ΔT: is the temperature difference between T_1 and T_2 (ºC), at steady state.

A: is the sample area (m^2).

The average value of thermal conductivity will be:

$$k = \frac{k_1 + k_2}{2} \tag{3.8}$$

Where: k_1 is the thermal conductivity for the first sample.

k_2 is the thermal conductivity for the second sample.

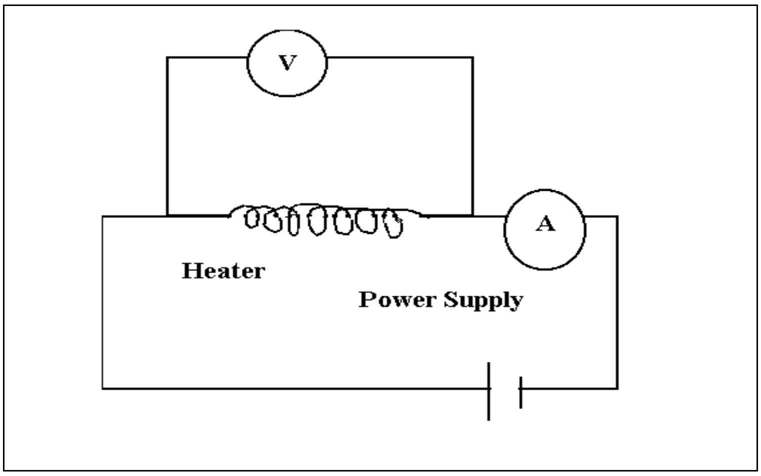


Figure (3.8): The circuit of thermal conductivity measurements.

CHAPTER FOUR
RESULTS & DISCUSSION

The optical, electrical and thermal properties of PEO/NaI electrolyte composites, containing 0, 1, 2, 4, 6, 8, 10, and 15% NaI by weight were studied through measurements and determination of some physical parameters such as the optical gap, the energy gap tails, refractive index, dielectric constant, AC electrical conductivity, relaxation time, thermal conductivity, and thermal activation energy at different measuring conditions.

Studies on the electrical and optical properties of polymer electrolyte have attracted much attention in view of their application in electronic and optical devices like electrochromic display devices, supper capacitors, fuel cell, gas sensors, solid state batteries etc.[V.Mohan, V.Raja, P.Bahrgav, A.Sharmam V.Rao, 2007]. The electrical and optical properties of polymers can be suitably modified by the addition of dopants or electrolytic substances.

4.1 Optical Results

Solids absorbed an amount of the incident light of intensity I_0 .and consequently optical transitions start when the energy of photon absorbed is a quantity higher than or equals to the forbidden energy gap. If the required energy is almost equal to the difference between the lowest level of conduction band and the highest level of valence band, electrons will transfer from the valence band to conduction band. At high absorption coefficient levels, where $\alpha\ (\omega) > 10^4\ cm^{-1}$, the absorption coefficient α for non – crystalline materials can be related to the energy of the incident photon energy ($\hbar\omega$) according to the following formula.

$$\alpha(\omega)\hbar\omega = B(\hbar\omega - E_{opt})^r \quad (4.1)$$

where B is a constant, E_{opt} is the optical energy gap and the exponent r is an index determined by the type of electronic transition causing the optical absorption and can take values 1/2, 3/2 for the direct and 2,3 for the indirect forbidden transitions [Saq'an and Zihlif,2003] , [Abu-Jamous, Zihlif, 2010].

Figures (4.1) and (4.2) illustrate the absorption and reflectance spectra of PEO composites with NaI particles content of neat PEO,1, 2, 4, 6, 8, 10 and15 wt. %. It is clearly shown that absorption decreases rapidly with increasing the wavelength up to 750 nm. Figure (4.3) shows graphs of the product of absorption coefficient (α) and photon energy ($\alpha\hbar\omega$) versus photon energy ($\hbar\omega$) at room temperature. The drawn straight lines obtained with r = ½ indicate that the electron transition is direct in k-space. Extrapolation of the linear portion of these curves gives the optical energy gap (E_{opt}) [Sbeih and Zihlif 2009] , [Mott, Davis, 1971].

Table (4.1) includes the determined values of (E_{opt}) which decrease with increasing the NaI content. At lower absorption level, in the range of (1 to 10^4) cm^{-1} , the absorption coefficient $\alpha(\omega)$ is described by Urbach formula [Urbach, 1953]:

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/\Delta E) \quad (4.2)$$

where α_0 is a constant and ΔE is the energy gap tail interpreted as the width of the tail of localized states in the forbidden band gap (Saq'an et al,2004) . Figure (4.4) presents the Urbach plots for the composite samples. The extrapolated tail width (ΔE)values are listed

in table (4.1), were determined by using the slope of the linear part of each curve and equation (4.2) as:

$$ln(\alpha) = \hbar\omega / \Delta E + ln(\alpha_0) \qquad (4.3)$$

The exponential dependence of α (ω) on photon energy ($\hbar\omega$) indicates that the absorption processes take place in the studied composites obey Urbach rule .These energy tails become smaller as the concentration of NaI decreases, which is consistent with that variation of the optical energy gap (E_{opt}). In general, the sum (E_{opt} + ΔE) represents the mobility gap and table (4.1) includes values of the mobility gap for different PEO electrolyte composites. The increments of the energy tail widths can be explained by the fact that increasing the NaI content may lead to the creation of, ionic complexes, disorder, and imperfections in the structure of the composites, a case that may increase localized states within the forbidden energy gap. The energy tails have smallest values due to neatness of the PEO structure and scanty impurities, which lead to decrease localized states within the forbidden band gap. This usually contributes to the increase in the optical energy gap [Elliot, 2000] ; [Sebeih, Zihlif, 2009].

Figure (4.5) shows the variation of the refractive index of the prepared PEO/NaI composites with the UV-visible wavelength, calculated from equation (3.4) and (3.5) which relate the refractive index (n) with the absorption coefficient (α) and the extinction coefficient (k) .The figure shows that the refractive index decreases rapidly at low wavelength (<500 nm). The dielectric constant (**ε'**) and dielectric loss (**ε''**) of the PEO/NaI composites were calculated from the relations (3.6).

Figures (4.6) and (4.7) show the variations of **ε'** and **ε''** as a function of radiation wavelength. Both constants decrease with increasing the wavelength. Figure (4.8) shows

the effect of NaI content on the refractive index and the dielectric constant, where both of them increase with increasing the concentration of the electrolyte NaI in the PEO matrix. The refractive index values ranged from 1.46 for pure PEO to 3.8 for 15 wt.% NaI composite, and the dielectric constant (**ε'**) ranged from 4.5 to 12 measured at 660 nm wavelength.

The observed increase in the dielectric constant, refractive index, and electrical conductivity due to incorporation of concentration of NaI salt particles in the PEO matrix was reported in many researches [Kurt, Turk, 2010] , [Dygas, Faraj, 2003] , [Mohan, Raja, 2007] Liu et al [Liu et al,2007] fitted a modeling relation between the dielectric constant and filler content based on an effective – medium theory (EMT), which relates the inter-phase particles, polymer matrix, and the composite morphology [Mohan, Raja, 2006], [Bhargav, Mohan and Rao, 2006]. The (EMT) model is expressed in form of Rao equation [Rao, 2000] as:

$$\varepsilon = \varepsilon_1[1+v_2(\varepsilon_2-\varepsilon_1)/(\varepsilon_1+n(1-v_2)(\varepsilon_2-\varepsilon_1)] \qquad (4.4)$$

where, ε, ε_1 and ε_2 are the dielectric of composite, PEO matrix, and discrete fillers , respectively, v_1.and v_2 are the volume fractions of continuous matrix and discrete fillers, n is a factor related to the morphology of filled particles. Figure (4.9) shows the fit of the EMT model of equation (4.4) to our PEO/NaI composites prepared via the casting method. The model fit predicts properly the increase of the dielectric constant ($\acute{\varepsilon}$) of PEO/NaI composites with increasing the filler concentrations, especially at lower NaI filler concentrations.

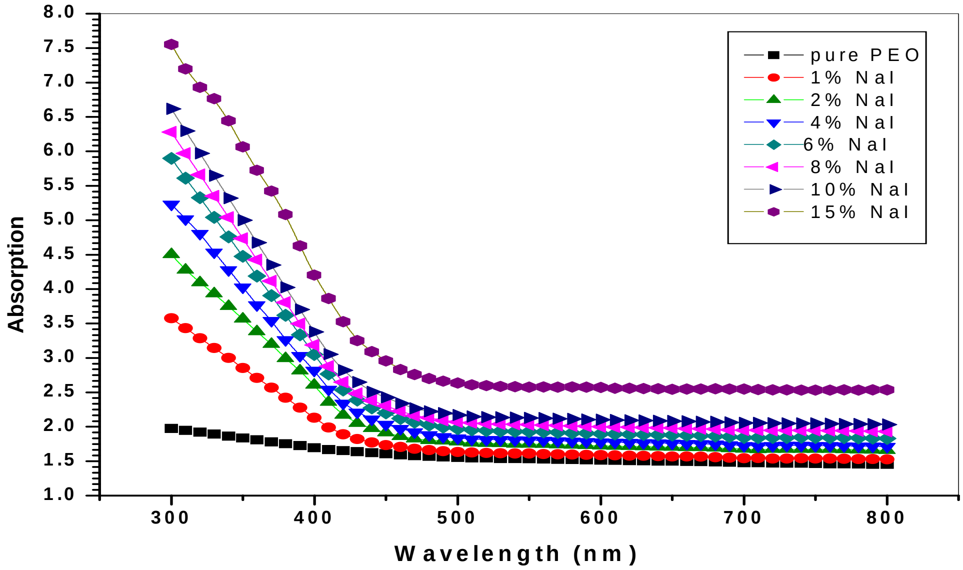


Figure (4.1) : Absorption spectra for PEO/ NaI composites.

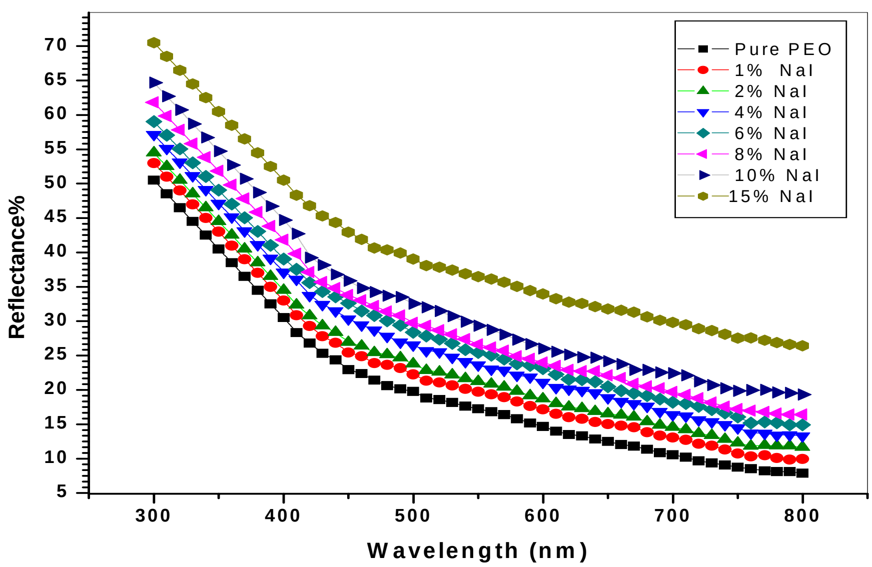


Figure (4. 2): Reflectance spectra for PEO/NaI composites

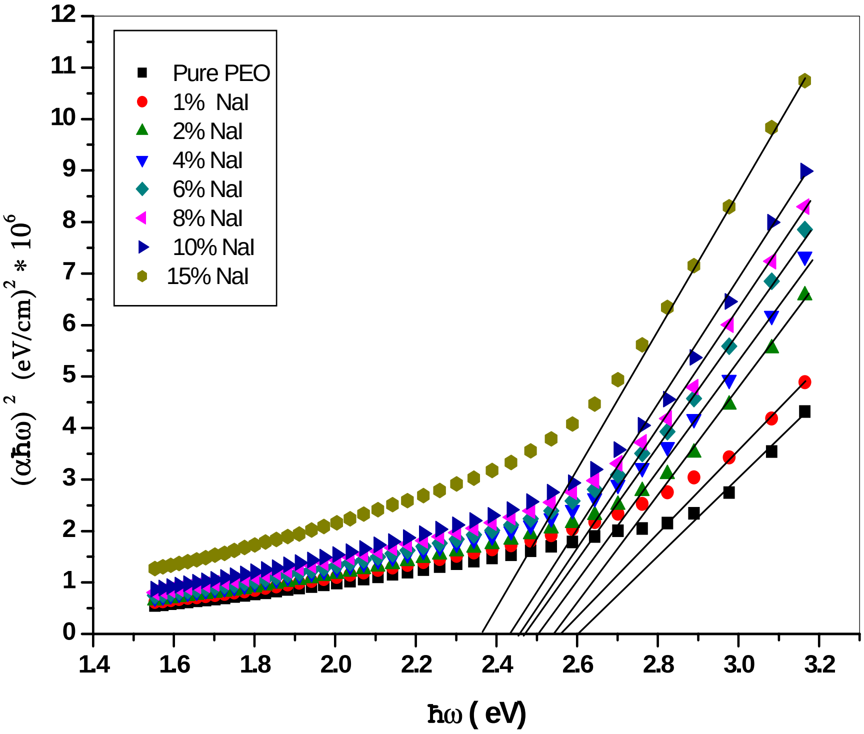


Figure (4.3) : $(\alpha\hbar\omega)^2$ versus the photon energy for PEO/NaI composites.

Table (4.1) : Optical energy results forPEO/(NaI) composite films

Composite	E_{opt} (eV)	ΔE (eV)	$E_g + \Delta E$ (eV)
Pure PEO	2.60	0.34	4.94
1 wt.% NaI	2.56	0.36	2.92
2 wt.%	2.54	0.37	2.91
4 wt.%	2.50	0.40	2.90
6 wt.%	2.48	0.41	2.89
8 wt.%	2.46	0.42	2.88
10 wt.%	2.44	0.43	2.87
15 wt.%	2.36	0.50	2.86

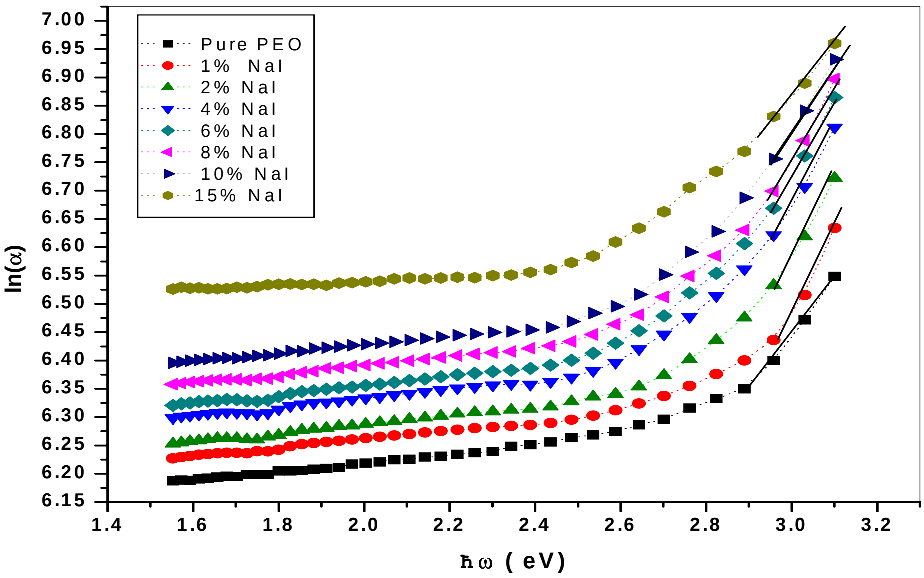


Figure (4.4): Urbach plot of Ln(α) versus the photon energy for PEO/NaI composites.

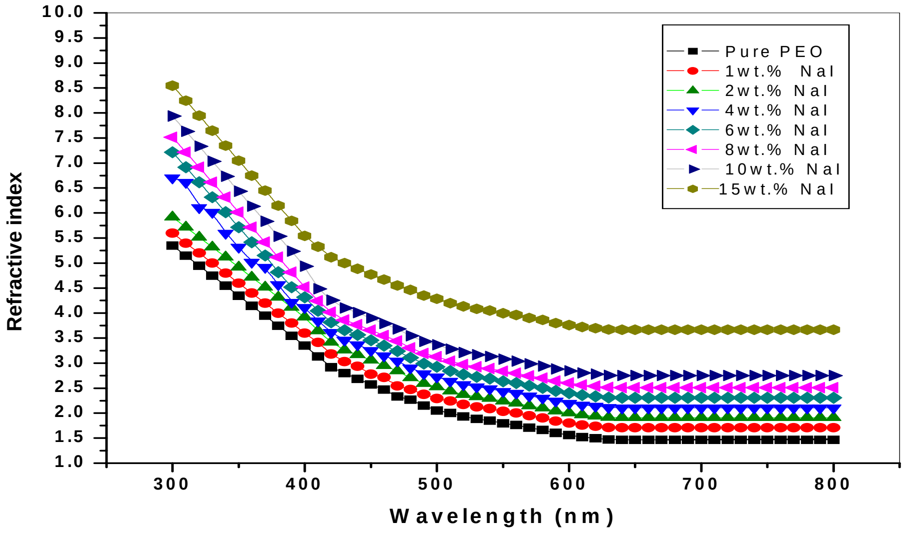


Figure (4.5) : Refractive index versus the UV- radiation wavelength.

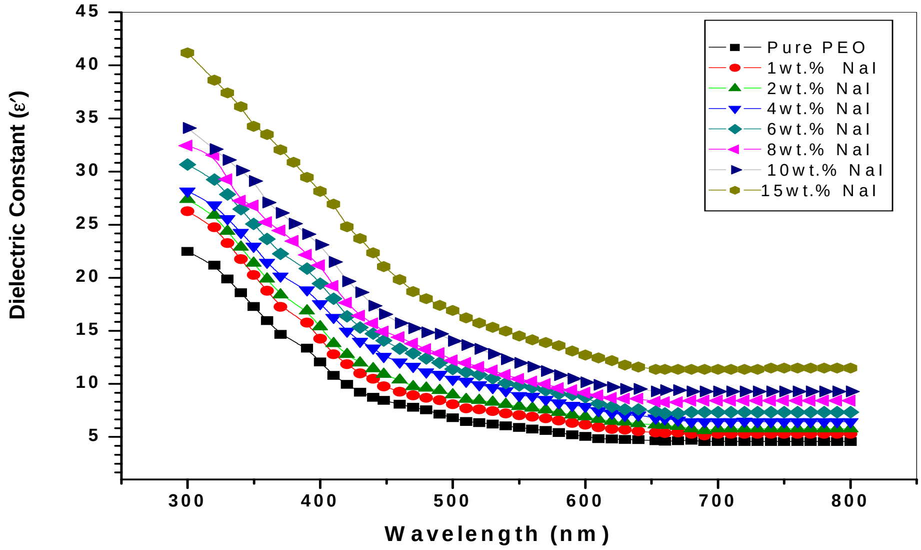


Figure (4.6) : The dielectric constant (ε') versus the wavelength.

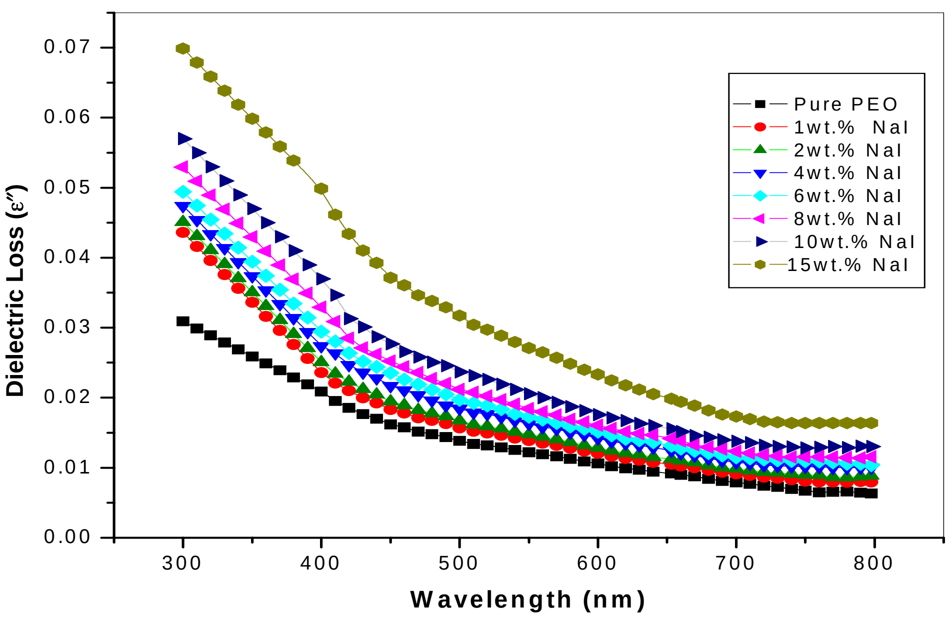


Figure (4.7) : The dielectric loss (ε'') versus the wavelength.

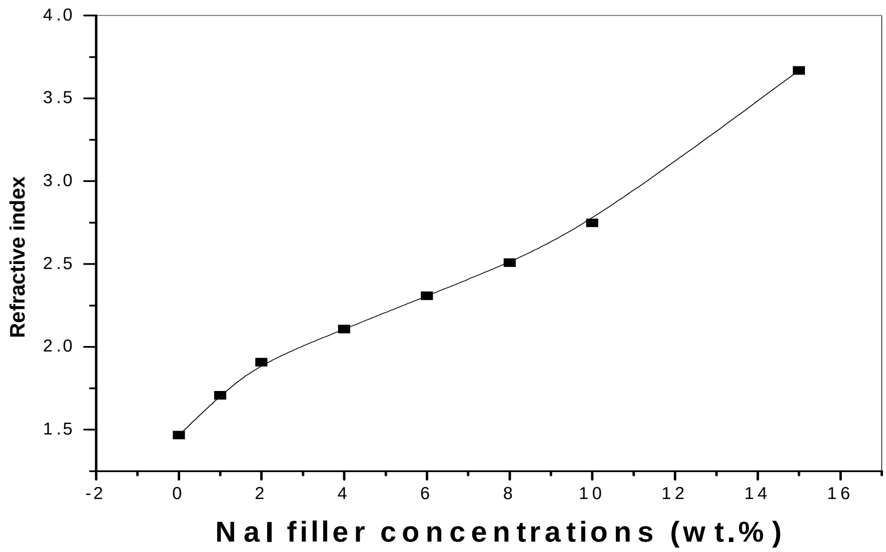


Figure (4.8) : The dependence of the refractive index on NaI concentrations.

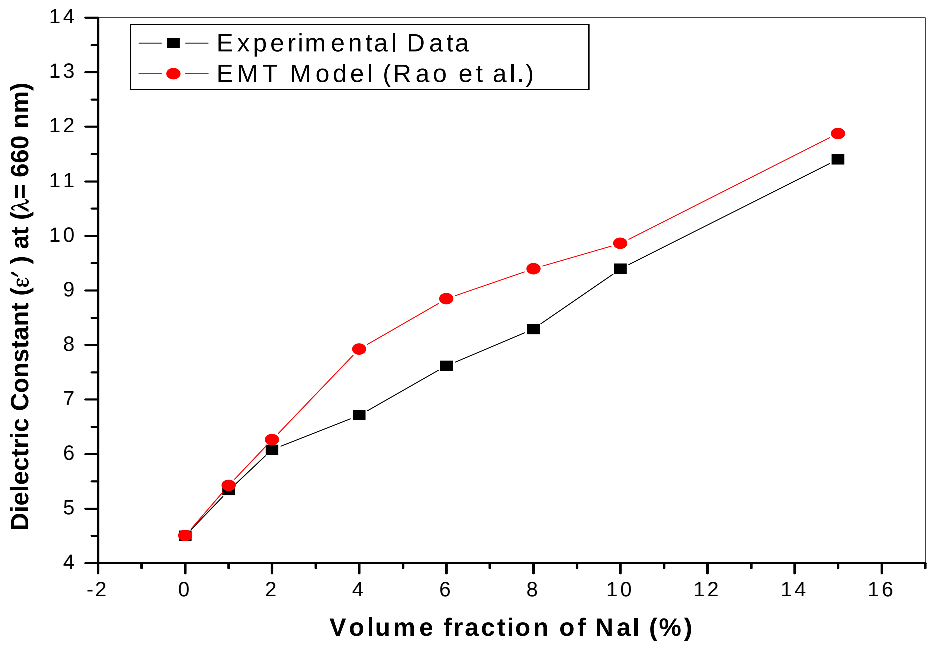


Figure (4.9) : The fit of EMT model: dielectric constant as a function of NaI concentration.

4.2 Electrical Results

Studying the electrical and dielectrical behavior by the powerful impedance technique is a promising method to characterize the material properties and to be utilized in modern technologies. The NaI filler added to PEO matrix to form solid electrolyte films is being explored to assess the role of this filler in the ionic conduction process when an electric field is applied. Electrical conduction in polymers has been studied aiming to understand the nature of the charge transport in these materials [Agrawal, R. C , Pandey, G. P. , 2008].

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4.2.1 The dependence of electrical properties on the applied field frequency

Impedance measurements have been performed on PEO/NaI composites in the range of frequency from 30 kHz up to 5 MHz.

Figure (4.10) shows the dependence of phase angle (φ) (phase difference between voltage and current), on frequency of the applied field for specimens of different NaI concentration and neat PEO. The phase angle (φ) is always negative; indicating that the bulk material can be made of capacitive and resistive networks. i.e., RC circuits. [AL-jamali, 1998] , ranged from – 89.63º for pure PEO, and – 77.3 for 15 wt.% NaI electrolyte system at 30ºC and frequency value equal 2000 kHz . (φ) decreases with increasing frequency. This figure shows that the change of phase angle (φ) toward low negative values with increasing NaI content indicating that the films become more resistive than capacitive. The AC electrical measurements are generally analyzed interm of equivalent electric circuits, carefully selected to be simple and logic. The circuits have frequency independent elements composed of a resistor and capacitor. The change of phase angle toward higher

negative values at high frequencies indicates that the material becomes more capacitive than resistive [Abu-Jamous, Zihlif, 2010].

Figure (4.11) shows the variation AC impedance (Z) per unit thickness as a function of frequency at room temperature for specimens of different NaI concentration and neat PEO. In general, the figure shows that the impedance decreases with increasing frequency. The high impedance values at low frequency, which mean more resistive behavior, are due to space charge polarization in samples, some structural defects (phase boundaries, grain accumulations) and electrode polarization effects [Sa′qan and Zihlif,2003; Nofal,2008]. On the other hand, the rapid decrease of impedance values indicates a response of the bulk with alternating electric field. This behavior may be attributed to reduction of the interfacial polarization effect, which may exist at the electrode-specimen surface [Abu Hijleh et al, 2000.Sbeih and Zihlif, 2009].

The dielectric constant (ε') values were calculated from equation (2.43) and plotted against frequency at room temperature for the eight composite specimens as shown in Figure (4.12). In general, a very slight decreases in ε' was observed with increasing frequency. The decrease of ε' with increasing frequency may be explained on the basis of space charge polarization (Wagner-Maxwell effect) which slightly enhances and compensates for the decrease caused by the orientational polarization [Jawad, 1993].The dielectric constant of the composite samples is higher than that of pure PEO, this increase is expected, since the dielectric constant of NaI is more than that for PEO. The observed improvement in the insulation property of the prepared composites, as we have seen from the increase of the dielectric constant with increasing the NaI concentration, is attributed to superior compatibility between the polymeric matrix and filler.

Figure (4.13) shows the behavior of the dielectric loss (ε") which represents the dissipated energy by the composite and was calculated from equation (2.44), against frequency at room temperature for the eight specimens, is represented in. At low frequencies, ε" has high value and then it starts to decrease at higher frequencies. The low frequency dispersion in ε" is attributed to the charge carriers, which leads to large losses at lower frequencies [Jonscher,1983].

From the dielectric constant (ε') and the dielectric loss (ε"), one can observe a frequency dependence, especially at low frequency, which reflects the behavior of the polar materials [Anderson,1964]. It is clearly seen that both (ε') and (ε") decreases with the frequency of the electric field. These results suggest that polar entities of the NaI and of the polar semicrystalline polymers i.e., dipole rotation or polar polarization, the PEO/NaI composites are effectively operating under the electric field [Nofal, 2008].

The AC- conductivity (σ_{AC}) for an ionic electrolyte materials was calculated from the equation (2.45), and plotted versus frequency for the specimens as shown in figure (4.14).The figure shows clearly that σ_{AC} value increases with increasing the applied frequency and NaI concentration [Ziadat, 2005]. This increasing in σ_{AC} is expected, since at higher applied field, more ions and charges are moved, resulting in enhancement of the ion conduction process. This result supports the well known fact that the bulk AC conductivity is induced at high frequency range as reported by many researches[Nofal,2008] . It can be conclude that the ionic conduction is enhanced at higher NaI content and higher applied frequency.

Generally, the observed enhancement in the dielectric constants and AC-conductivity is attributed to the ionic interaction taking place in the bulk of the solid electrolyte. The bulk

effect creates an excess in movable ions and charged particle, especially the impurities [Y. Ramadin, S. Saqan, and A. Zihlif, 2000] .

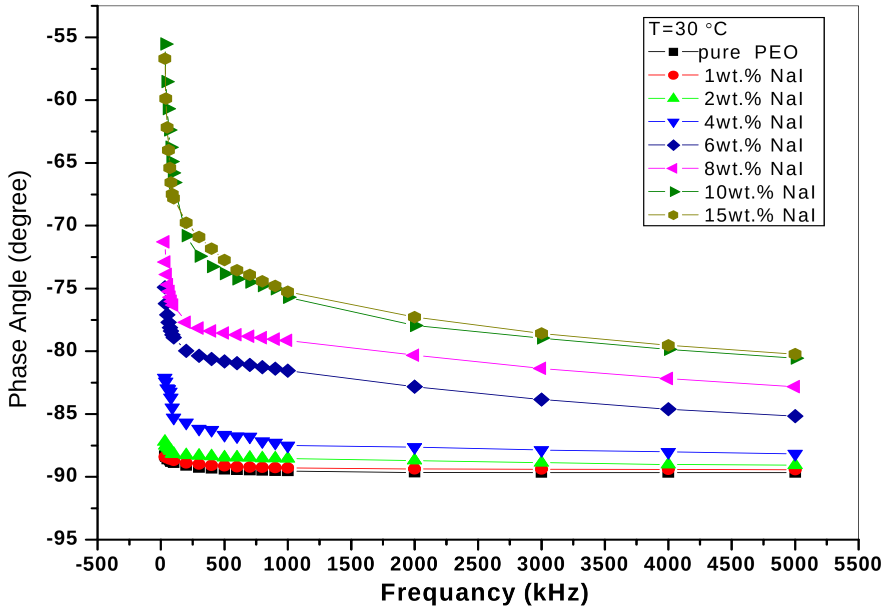


Figure (4.10): Phase angle versus frequency for NaI/PEO composite at T=30 ºC.

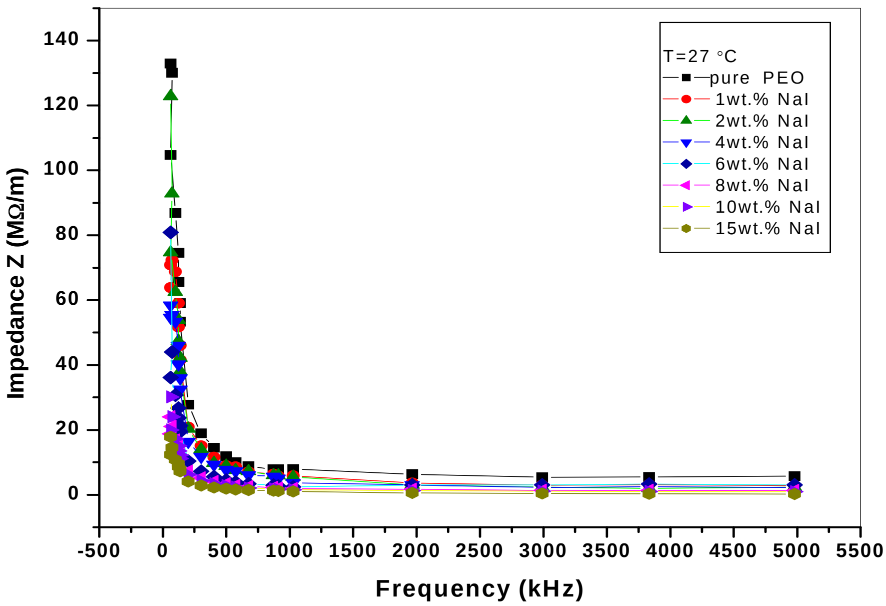


Figure (4.11): Impedance versus frequency for PEO/NaI composites at T=27 ºC.

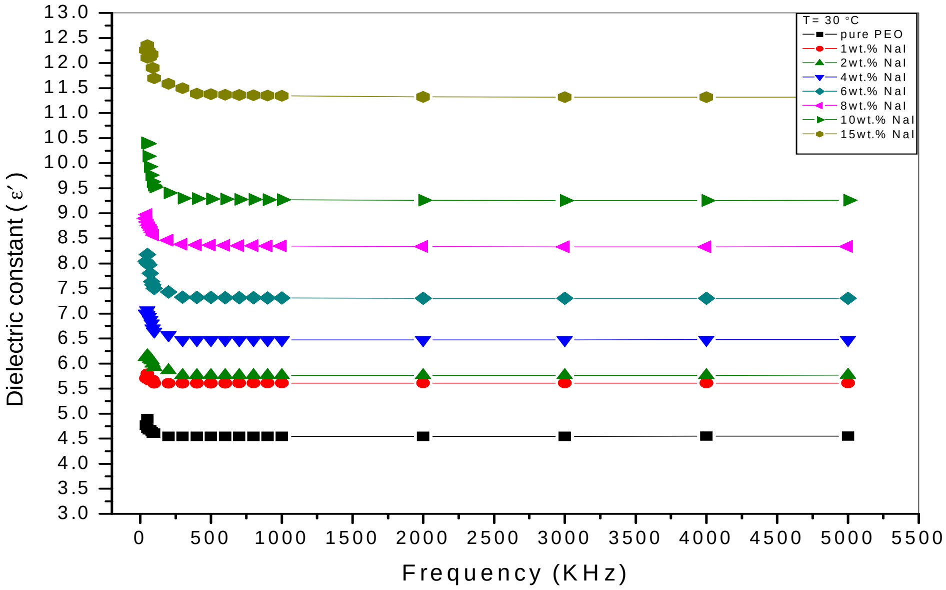


Figure (4.12): Variation of dielectric constant with frequency at T=30 ºC for NaI/PEO composite

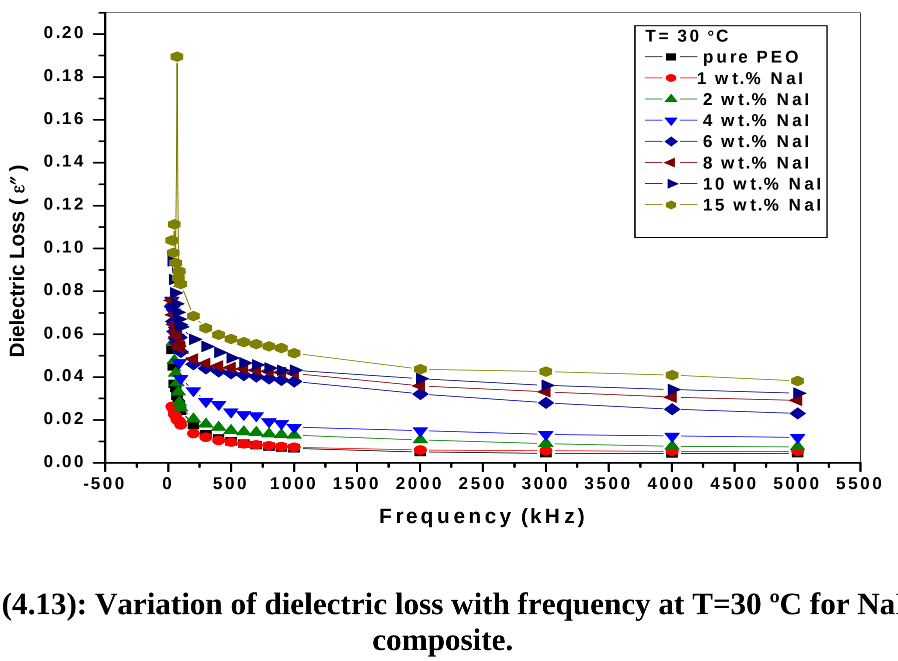


Figure (4.13): Variation of dielectric loss with frequency at T=30 ºC for NaI/PEO composite.

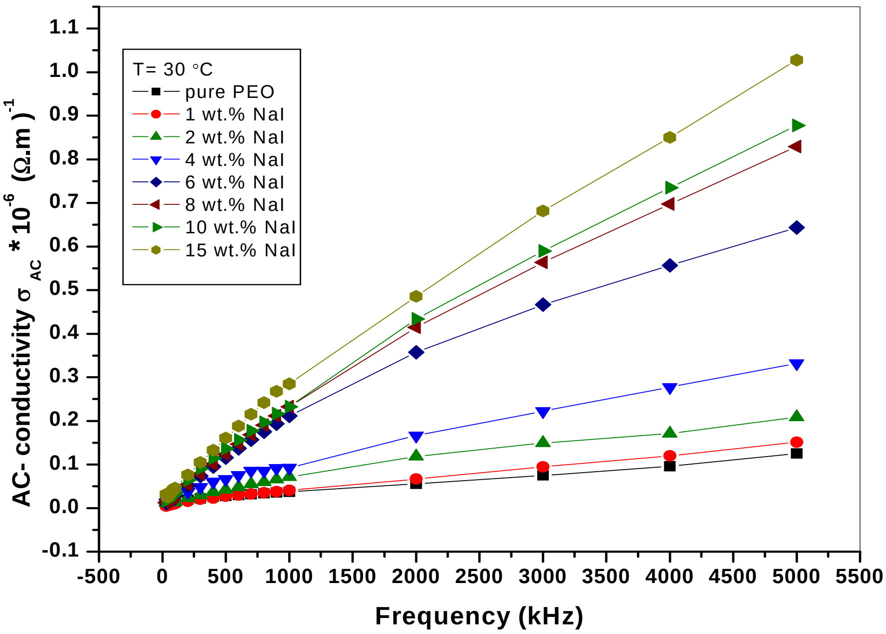


Figure (4.14): The AC conductivity of composites as a function of frequency.

4.2.2 Dependence of Electrical Properties on NaI Concentration

Figure (4.15) shows the dependence of the AC impedance (per unit length) on the NaI concentration at different frequencies (200 kHz, 400 kHz, 600 kHz, 800 kHz, and 1000 kHz) at room temperature for the prepared composites. When the filler content increases, Z decreases. The observed decreases in impedance values with increasing NaI content is due to protonic migration transporting the ethereal oxygen of PEO and impurities in the NaI filler. These sources may lead to higher electrical conduction in the filled films [Y. Ramadin, S. Saqan, and A. Zihlif, 2000]. Figures (4.16) and (4.17) show the variations of the real dielectric constant(ε') and the dielectric loss(ε'') on the NaI filler concentration measured at different frequencies. The dielectric constant (ε') decrease with increasing the

applied frequency, while increases greatly from about 4.5 for pure PEO to a value 11.5, with increasing the filler concentration up to 15wt.%. Similar behavior for the dielectric loss (ε''). The high enhancement in dielectric constant (ε') with NaI concentration is mainly due to ions contribution, while the high values of (ε') at low frequency range are due to space charge polarization (Wagner- Maxwell effect).

Figure (4.18) shows the variation of AC conductivity (σ_{AC}) with NaI concentration. The increase in AC conductivity was observed as a function of filler content at different frequencies (100kHz, 200 kHz, 300kHz, 400 kHz, 500 kHz, and 600 kHz) which means that PEO/NaI composites become less resistive with the increase of the filler content. The (σ_{AC}) is nearly constant up to 1.5 wt.%, after that it increases rapidly with increasing the NaI concentration. The value of 1.5 wt.% filler content can be considered a critical one and called a percolation threshold for the prepared thin films composite. The increase in ionic conductivity with the increase of the content of the NaI is attributed to increase ionic charge carrier concentration. The motion of ions in solid polymer electrolytes is a liquid- like mechanism, by which the movement of ions through the polymer matrix is assisted by the large amplitude of the polymer segmental motion. The segmental mobility of polymer chains is much higher in amorphous region than the crystalline. In general, conductivity increases as the degree of crystallinity decrease or, in other words, as the flexibility of the polymeric backbone increases. The continuous increase in conductivity of polymer is attributed to decrease in the degree of crystallinity and increase in the amorphicity.[V. Mohan, V. Raja, A. Sharma, 2006].

The ionic size is also one of the factors in increasing mobility of ions. Hence the conductivity of the polymer increases. Since Na^+ is a fast conducting ion in a number of crystalline and amorphous materials, its incorporation in a polymer system may be expected to enhance its electrical and optical performance. The marked increases in electrical conductivity with increasing concentration of dopant salt makes it possible to consider this electrolyte system for electrochemical device applications [V. Mohan, V. Raja, A. Sharma, V. Rao,2007].

A correlation between the observed energy gap (E_{opt}) and the electrical conductivity (σ_{AC}) can be drawn from table (1) and figure (4.18). it can be seen that the (σ_{AC}) increases and the (E_{opt}) decreases with increasing the NaI content. This behavior is physically consistent, since the PEO/NaI composite becomes more ionic.[Y. Ramadin, S. Saqan, A. Eid, M. Ahmad and A. Zihlif, 2000].

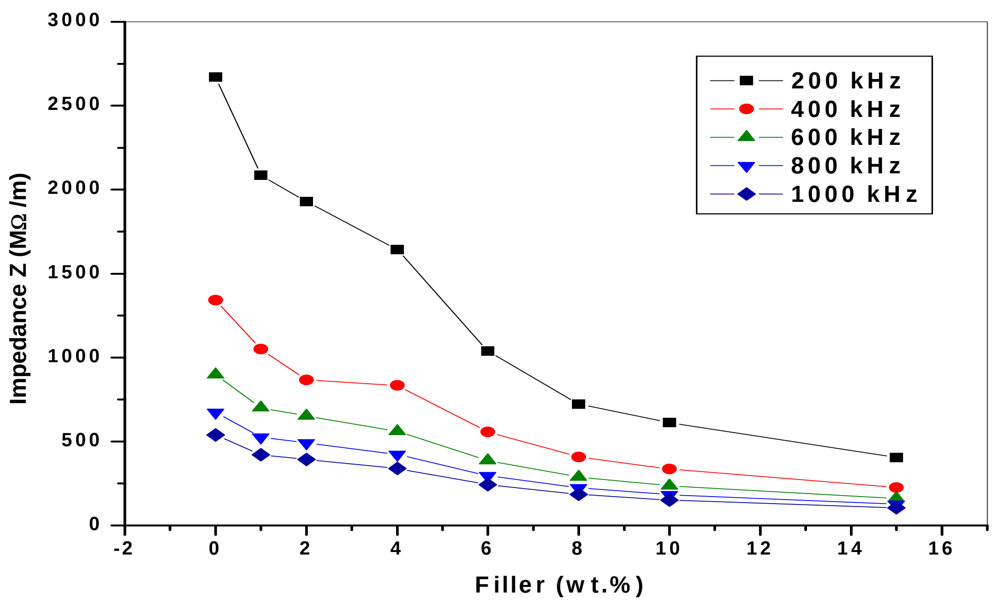


Figure (4.15): Variation of impedance with NaI concentrations

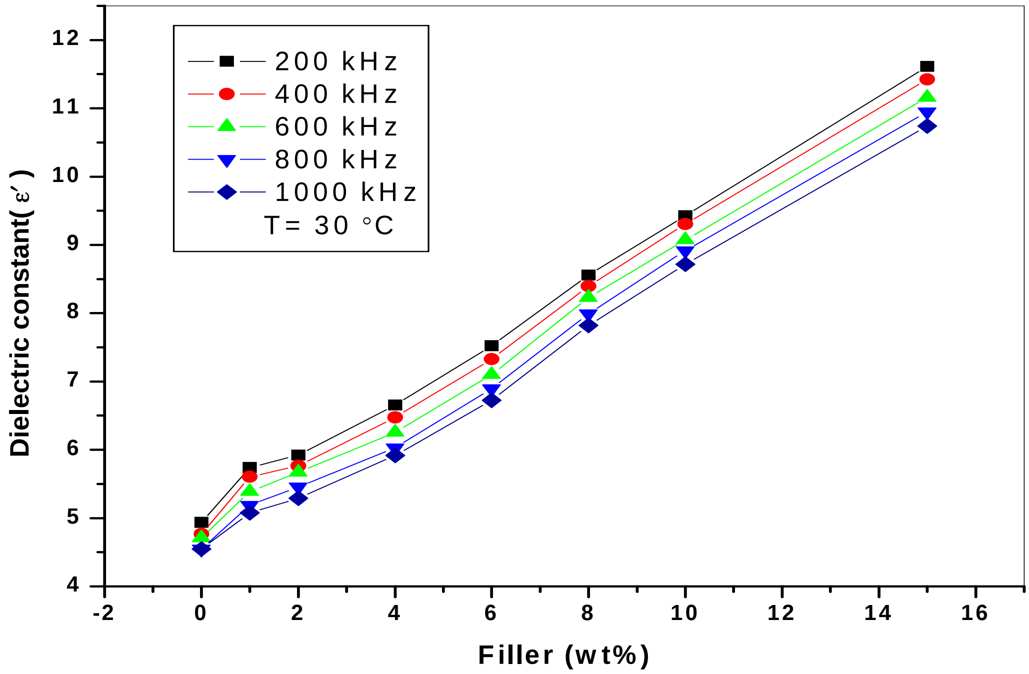


Figure (4.16): Variation of dielectric constant with NaI concentrations

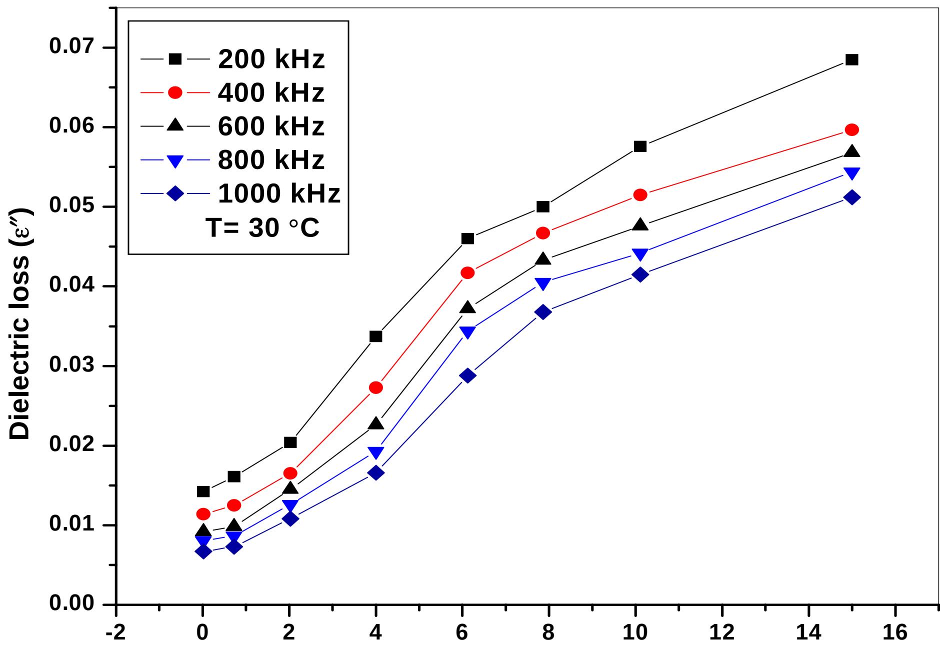


Figure (4.17): Variation of dielectric loss with NaI concentrations

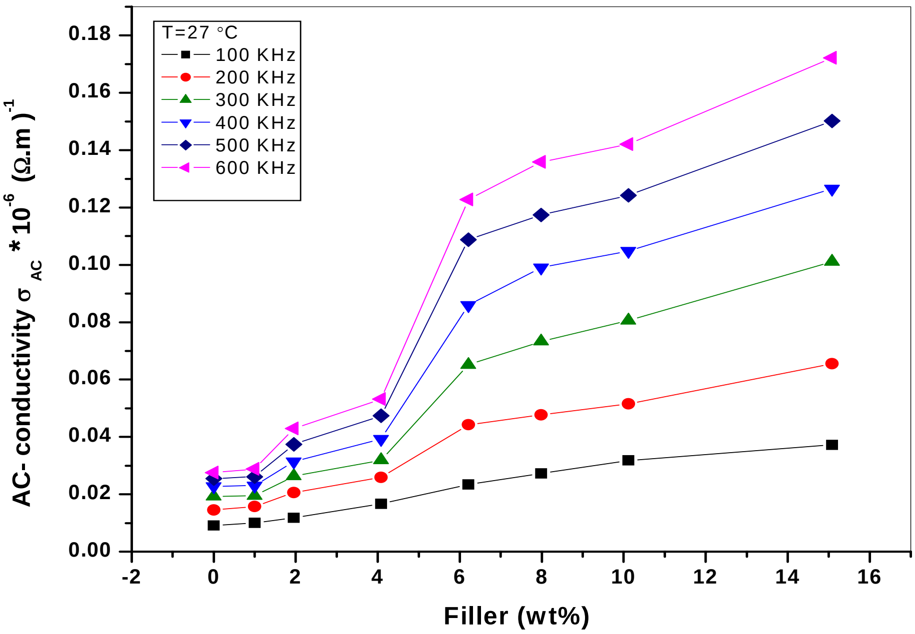


Figure (4.18): Variation of AC conductivity with NaI concentrations

4.2.3 Dependence of Electrical Properties on Temperature

The thermo-electrical behavior of PEO/NaI composites is examined at temperatures (27°C , 30°C , 40°C , 45°C ,50°C , and 60 °C) under different frequencies. The variation of impedance (Z) with temperature at different concentrations of the NaI is shown in figure (4.19). It is clear that impedance decreases with increasing temperature. This may be explained in terms of certain events such as charge carriers generation, increasing charge mobility, and closing up the energy gap. These processes affect the charge carriers transport in the composite bulk, and may produced from superposition of polarization and conduction current effects. The polarization current depends on temperature, where the decay time of polarization is shortened by increasing temperature. This behavior proves

that the conductivity is increasing as temperature increases, similar to semiconducting and ionic solids behavior (Elliott, 2000).

The plots of the dielectric constant (ε') and dielectric loss (ε″), calculated from equations (2.43) and (2.44) versus temperature at different NaI concentrations are shown in figures (4.20-4.21) ranged from 27 ºC up to 60 ºC for the polymer electrolyte of 8wt.% and 6wt.% NaI filler. The observed dielectric constant (ε') increases largely from about 7.5 to 13.5. This observed increase in dielectric constant (ε') with increasing temperature caused by a decrease in the space charge (interfacial) polarization and to build up of ionic aggregates or clusters inside the solid polymer electrolyte by heating. An increase in (ε') with temperature is observed, but it increases much faster at high temperatures. This suggests that when the temperature rises, the orientation of dipoles is facilitated and relaxed at high temperatures, and hence increases the dielectric constant. This is similar to what normally observed in polar polymer as PEO [Ayad, 2006].

Figure (4.22) represents the AC conductivity (σ_{AC}) versus temperature for the 6 wt. %t NaI composite. It was found that AC-conductivity values increase as temperature increases at all frequencies, and this is due to electron and impurity activation that increases with increasing temperature, and to ionic and molecular mobility of PEO stimulated at high temperatures, i.e., the flow of electrons or charged ions established between the electrodes with high relative motion of polymer chains and thus leading to higher conduction . which is relatively similar to ionic and semi conducting materials.

The sudden increase in conductivity versus temperature plots may be attributed to the transitions from crystalline/ semicrystalline phase to amorphous phase. The increasing in the conductivity with temperature is interpreted in terms of a hopping mechanism between

coordination sites, local structure relaxation, and segmental motion of the polymer. As amorphous region increases, however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favors the interchain and interchain hopping movements, and the conductivity of polymer thus becomes high. [Mohan, 2006].

The rapid increase in σ_{AC}, is mainly due to increasing the concentration of charge carriers as a result of increasing structure defects, which can create new energy levels inside the forbidden energy gap ; and also, electronic mobility is stimulated in impurities at high temperatures.

Because the conductivity – temperature data obey Arrhenius relashinship, the nature of cation transport is quite similar to that occurring in ionic crystals, where ions jump into neighboring vacant sites and interchain spaces and hence increase the ionic conductivity [Mohan, 2007].

The electrical conduction mechanisms operating as a function of frequency and temperature can be grouped as follows:

- AC-charge conduction due to impurities existing in both the polymeric matrix and the filler.
- Maxwell-Wagner buildup of interfacial charges at the PEO/filler interfaces.
- Hopping of charge carriers over smaller barrier heights.

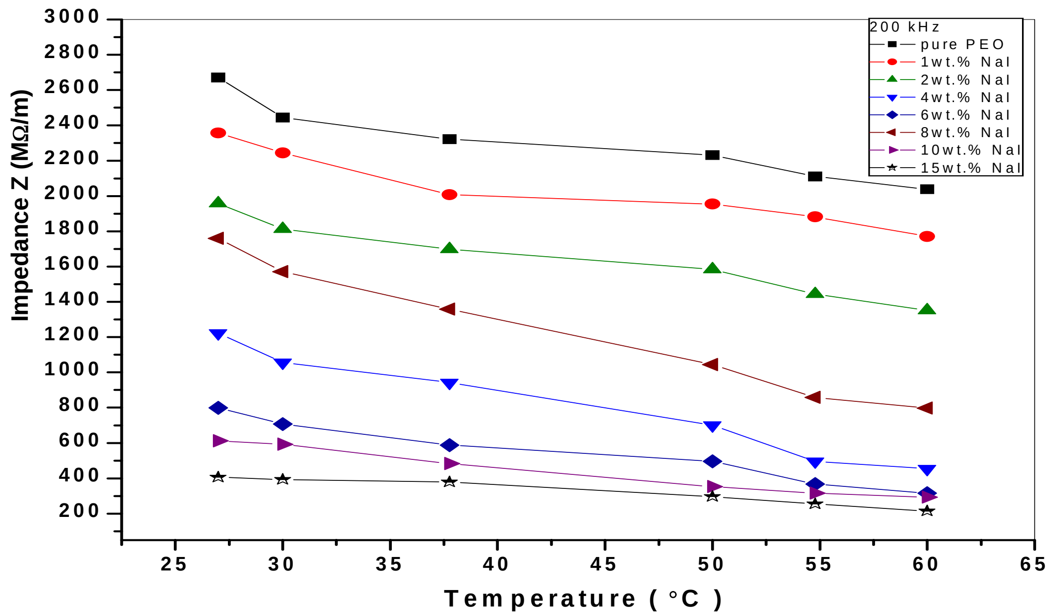


Figure (4.19): Impedance against temperature at frequency 200 kHz for PEO/NaI composites.

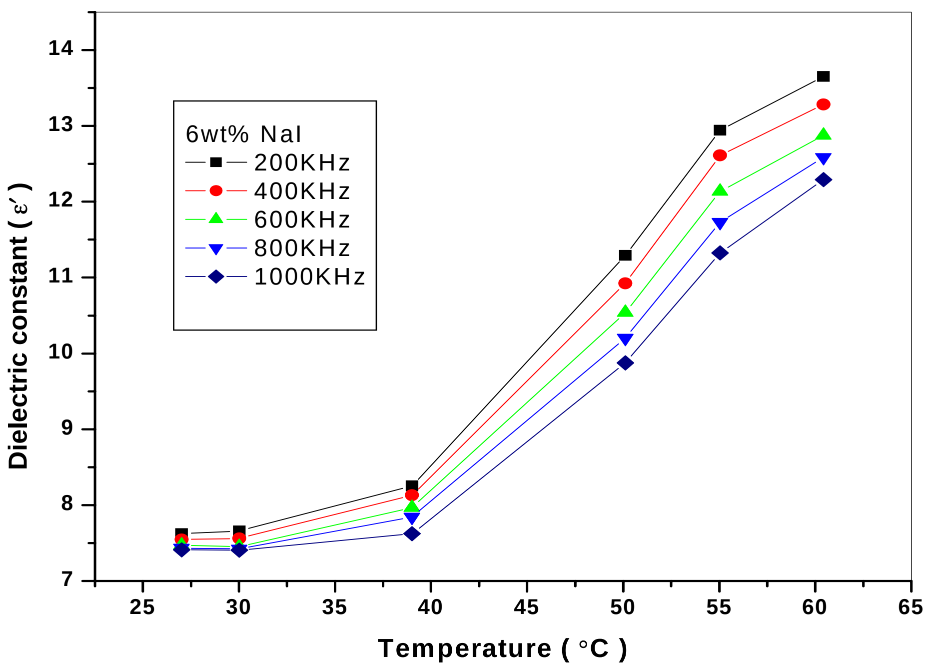


Figure (4.20): Dielectric constant vs temperature for different frequencies for 6 wt.% NaI.

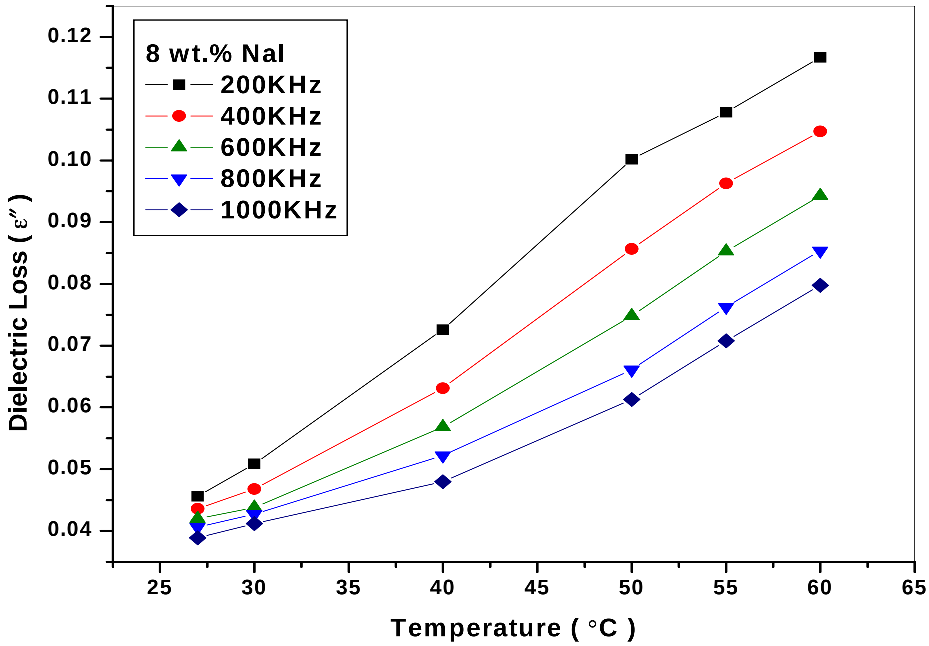


Figure (4. 21): Dielectric loss vs temperature at different frequencies for 8 wt.% NaI

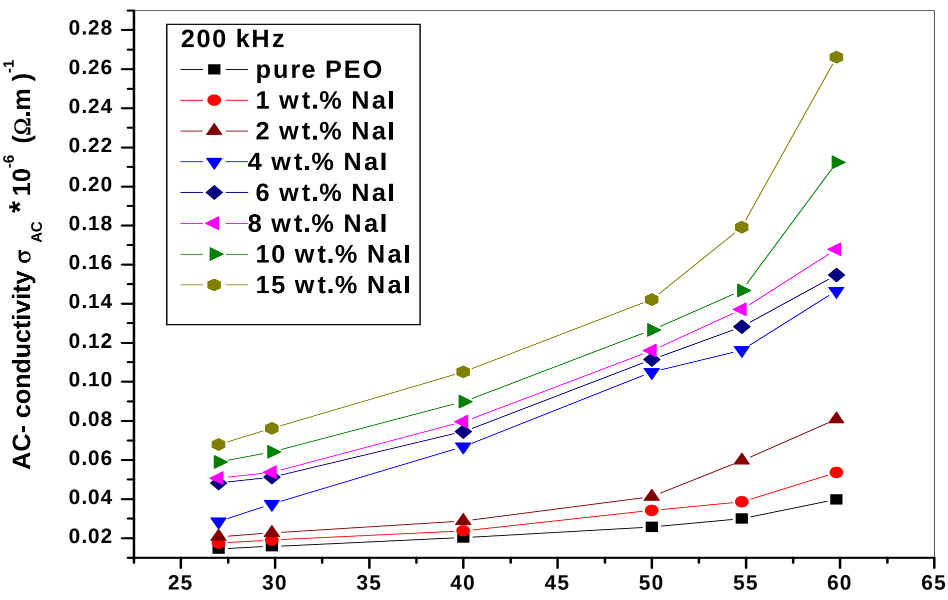


Figure (4.22): AC-conductivity vs temperature for PEO/ NaI composites

4.2.4 AC Conductivity Model at Different Temperatures

The universal relation of the AC-conductivity is given by the power law form as**:**

$$\sigma_{AC}(f) = \sigma_{DC} + B f^{m} \qquad (4.7)$$

where B and *m* are coefficients, f is the frequency of the applied field (Hz), σ_{DC} is the DC conductivity of the material and σ_{AC} is the AC conductivity of the material in $(\Omega.m)^{-1}$. At higher frequencies the conductivity increases as a power of frequency with exponent $0 < m < 1$. In this case B and m are temperature dependents. Analyzing the AC conductivity results of the PEO/NaI composites of concentration (8 wt.%) was done by plotting common logarithms Log (AC conductivity) versus Log (frequency) for each temperature, as shown in Figure (4.23). Based on this figure, it can be assumed that the equation above can be simplified in our temperature range to

$$\sigma \approx B f^{m} \qquad (4.8)$$

From these figure we can estimate the coefficients *B* and *m*. The results are shown in Table (4.2) which shows that the values of B increase with increasing temperature [Atta, 2003] and all m values are close to 1.

Table (4.2): Estimated B and m coefficients for (8 wt. %) NaI composite

Temperature(^{0}C)	B× 10^{-11} $(\Omega.m)^{-1}$ $(Hz)^{-m}$	m
27 ºC	0.608	0.84
30 ºC	0.634	0.85
40 ºC	0.883	0.83
50 ºC	0.973	0.77
55 ºC	0.974	0.81
60 ºC	0.98	0.79

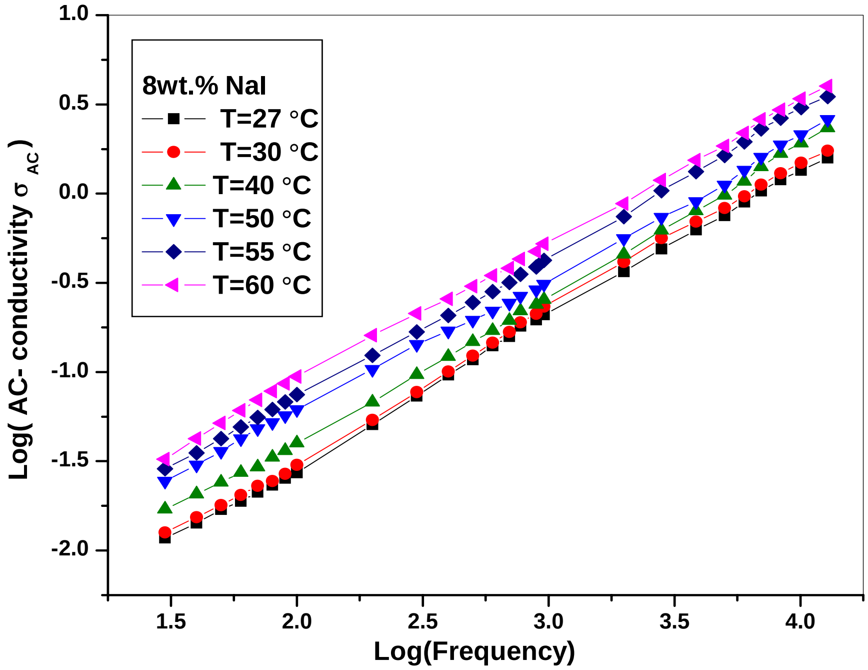


Figure (4.23): Variation of log (AC-conductivity) vs log (frequency) for 8 wt. % NaI composite

4.2.5 Cole-Cole Plots and relaxation time

Cole-Cole plots are usually used as a successful tool to analyze the dielectric data of dielectric materials. We use it here to characterize the dielectric behavior of the PEO/NaI composites and find the relaxation time of these samples at different temperatures [Anderson, 1964].

Figures (4.24- 4.30) shows Cole-Cole plots for dielectric loss ε" versus the dielectric constant (ε') for the composite sample of (4 wt. %) NaI content at different temperatures. The construction plane plots are distorted arcs exhibiting different electrical conduction processes with relaxation time (τ) spectrum.

Figure (4.30) shows that the values of both the dielectric constant (ε') and dielectric loss (ε") increase with increasing in temperature from 27^0 C to 60^0 C; this indicates that composite films become more conductive since the dielectric loss (ε") is proportional with AC-conductivity.

Figure (4.31) shows that the calculated relaxation time (τ) values decrease with increasing temperature, this may be attributed to ions and charges mobility, which increases as temperature increases as indicated previously. The increase in temperature will increase the energy of the dipoles in the sample, so the dipoles rapidly respond to the external electric field, i.e., increasing temperature decreases the relaxation time of the dipole rotation, [Sbeih and Zihlif, 2009]. Table (4.3)shows the calculated relaxation time(τ)

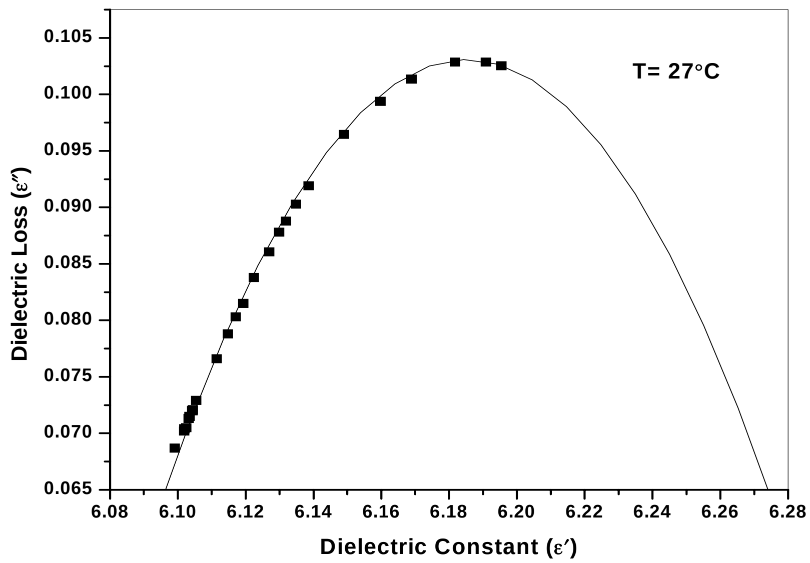


Figure (4.24): Cole-Cole plots for 4 wt. % PEO/NaI composite at T=27^0C

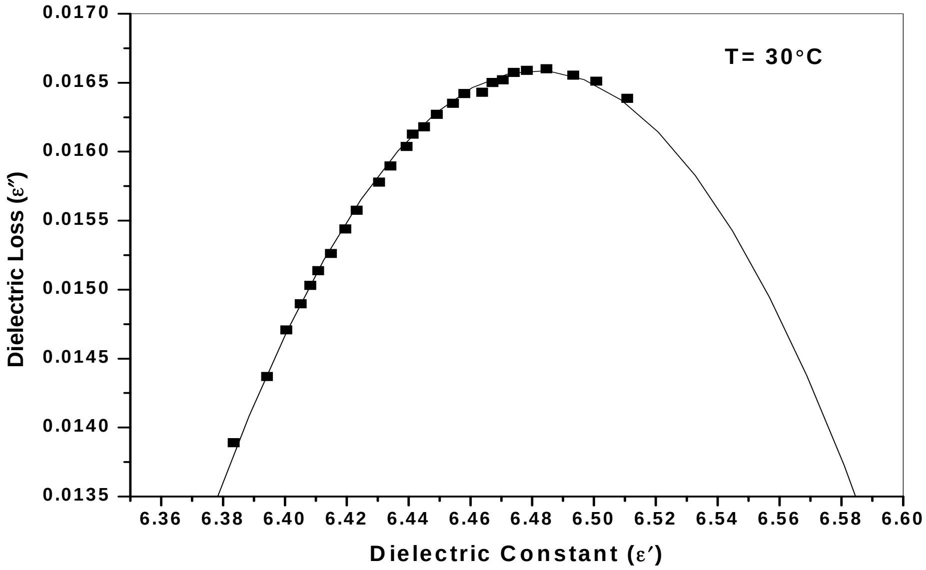


Figure (4.25): Cole-Cole plots for 4 wt. % PEO/NaI composite at $T=30^0C$

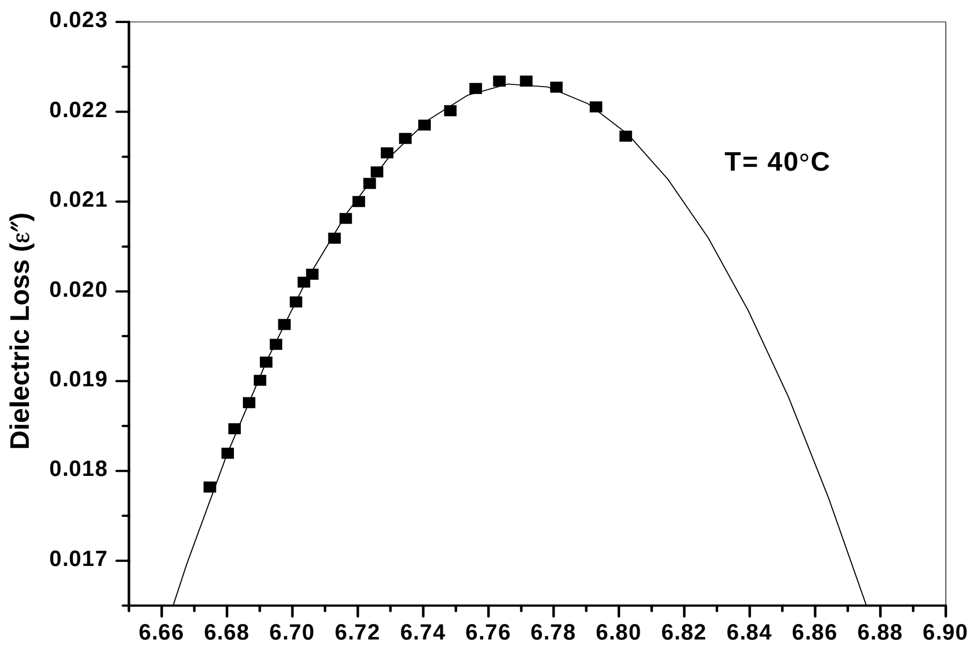


Figure (4.26): Cole-Cole plots for 4 wt. % PEO/NaI composite at $T=40^0C$

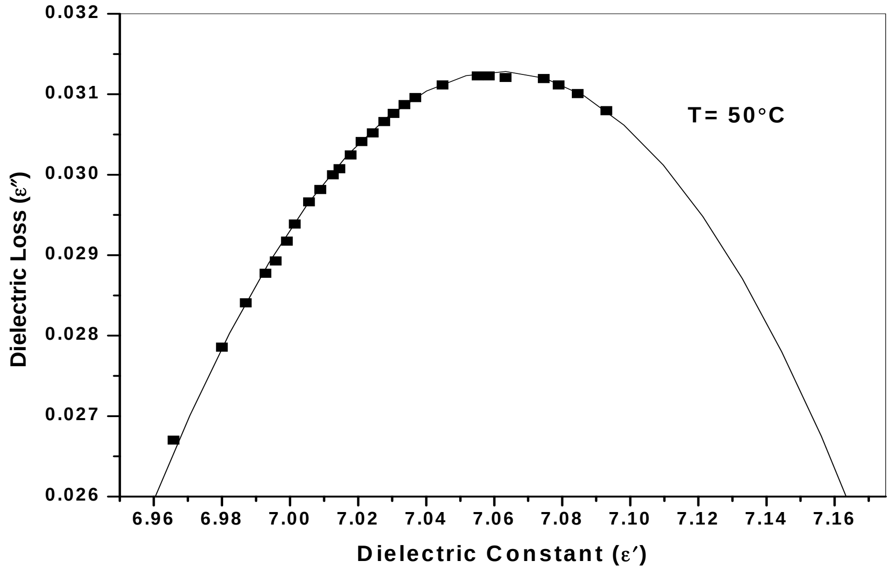


Figure (4.27): Cole-Cole plots for 4 wt. % PEO/NaI composite at T=50^{0}C

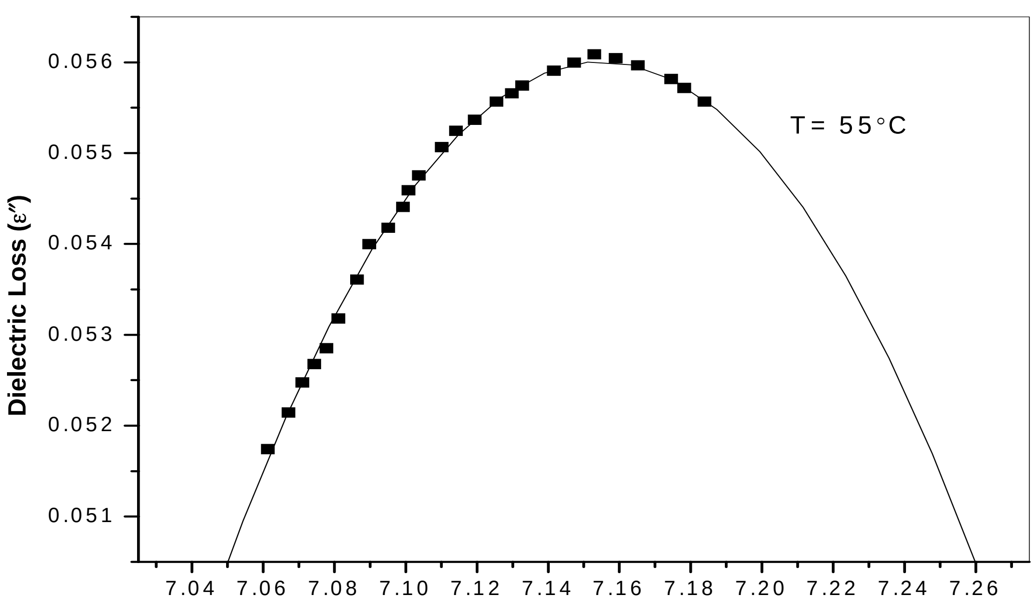


Figure (4.28): Cole-Cole plots for 4 wt. % PEO/NaI composite at T=55^{0}C

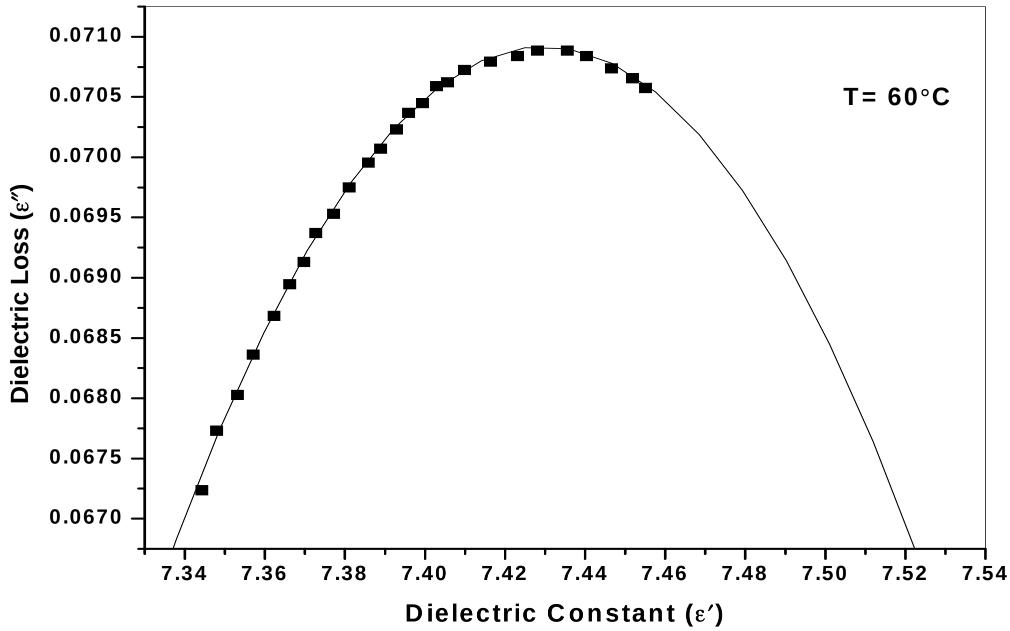


Figure (4.29): Cole-Cole plots for 4 wt. % PEO/NaI composite at $T=60^0C$

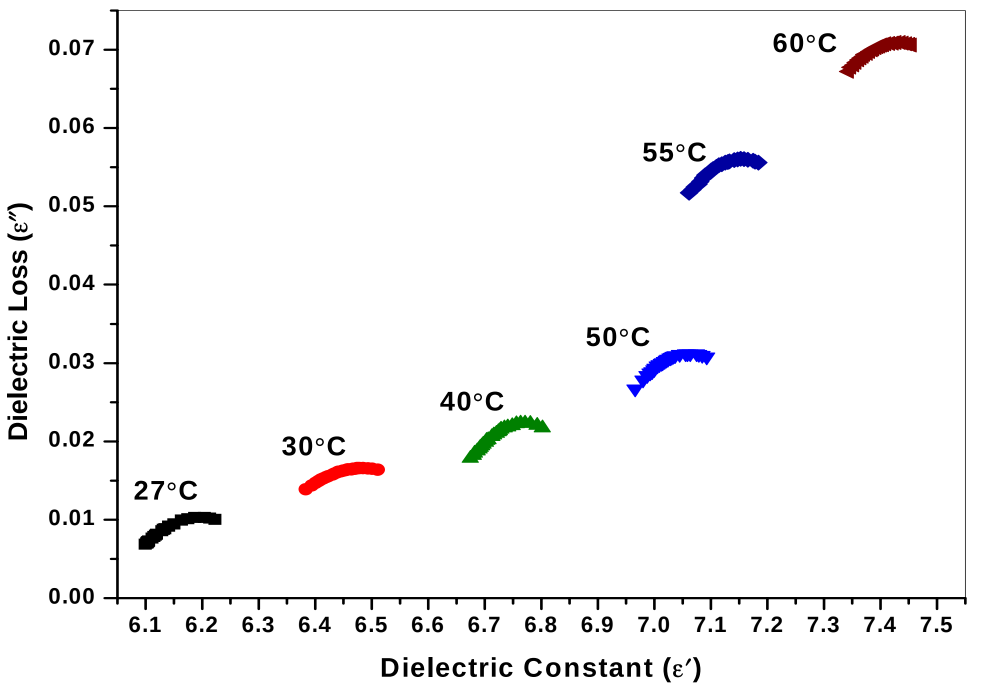


Figure (4.30): Cole-Cole plots for 4 wt. % PEO/NaI composite at different Temperature

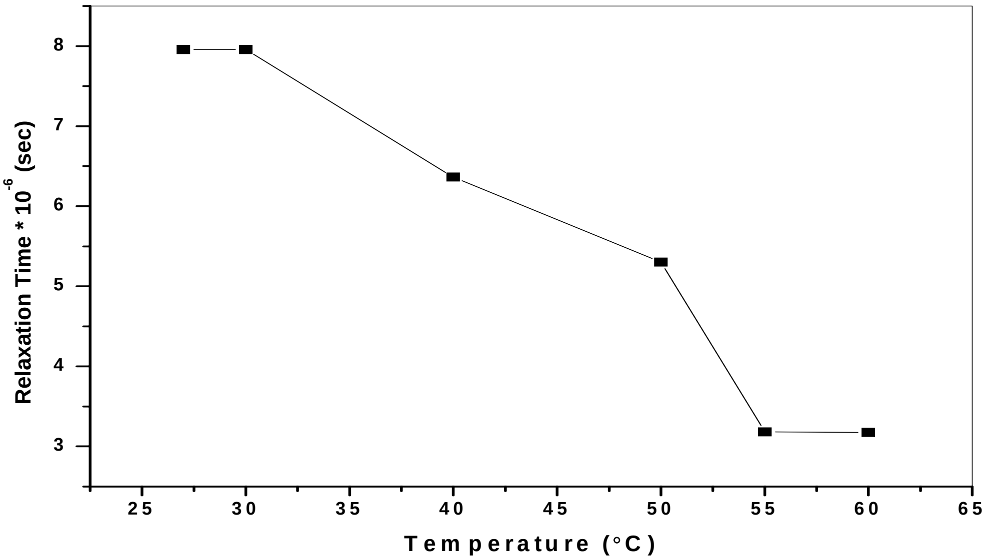


Figure (4.31): Variation of relaxation time with temperature for 4 wt. % PEO/NaI composite

Table (4.3): Relaxation time for 4wt.% NaI as a function of temperature.

Temperature (ºC)	Relaxation Time $\tau \times 10^{-6}$ (s)
27 ºC	7.955
30 ºC	7.950
40 ºC	6.364
50 ºC	5.303
55 ºC	3.182
60 ºC	3.175

4.2.6 Activation Energy Determination

The minimum amount of thermal energy that is required to activate ions, atoms, and molecules to conduction in which they can undergo physical transport is known as activation energy (E_a). The values of E_a were calculated from the slopes of the approximated straight lines obtained by plotting the natural logarithm of the conductivity (Ln σ_{AC}) versus (1000/T) for each sample at the frequencies (200, 400, 600, and 800 kHz) as shown in figures (4.32 - 4.39).

By using Equation of Arrhenius type (2.46) the E_a values were determined and inserted in tables (4.4 -4.11) which show the dependence of E_a on frequency for thermally activated conduction processes (ionic and electronic). It was found that the E_a decreases with increasing the applied frequency for all tested composites figure (4.40). The decrease in E_a reflects higher ionic mobility and enhancement in electrical conduction in the thin composite films membranes [Ahmad, *et al*., 1991].

Figure (4.41) shows that the activation value decrease with increasing the NaI concentration in a thermally activated process, the composites become more conductive as shown in figure (4.18). This observed decreases in E_a value implies that the energy of the prepared PEO/ NaI thin films becomes narrower due to creation of localized energy states by heating which enhances the ion mobility and ability of the electron to tunnel or hop easily from the valence band to conduction energy band. Similar observations were reported by Mohan *et. al.* on a study of the DC conductivity of PEO complexes with Fluorides , and attributed the increases in the conductivity to some structural transitions from crystalline phase of the polymer to amorphous phase. These events increase the amorphous region in the polymer PEO and produce more active segmental motion which

stimulates the electron hopping mechanism and thus the conductivity thus becomes high. In our present, the observed increase in conductivity and decrease in the activation energy values with increasing the NaI content or temperature can be dominated by the mobility in the localized states bridged by the doped NaI molecules in the amorphous regions existing in the solid polymer electrolyte. The low activation energy for sodium ion transport is due to the completely amorphous nature of polymer electrolyte that facilitates the fast Na^+ ions motions in the polymer network.[P.Bhargav, M.Mohan, Sharma, Rao, 2007]. Also, the iodine ions complexes contribute in the ionic conduction process takes place in the solid electrolyte composite [Abu Jamous, 2010].

Table (4.4): The activation energy for neat PEO

Frequency (kHz)	Activation Energy $\times 10^{-2}$ (eV)
200	48.56
400	45. 54
600	45. 28
800	44.50

Table (4.5): The activation energy for 1 wt. % NaI

Frequency (kHz)	Activation Energy$\times 10^{-2}$ (eV)
200	38.72
400	32.86
600	30.45
800	28.55

Table (4.6): The activation energy for 2 wt. % NaI

Frequency (kHz)	Activation Energy×10^{-2} (eV)
200	38.73
400	29.67
600	25.44
800	20.10

Table (4.7): The activation energy for 4 wt. % NaI

Frequency (kHz)	Activation Energy×10^{-2} (eV)
200	30.18
400	25.63
600	25.1
800	20.09

Table (4.8): The activation energy for 6 wt. % NaI

Frequency (kHz)	Activation Energy×10^{-2} (eV)
200	30.70
400	26.25
600	23.37
800	23.28

Table (4.9): The activation energy for 8 wt. % NaI

Frequency (kHz)	Activation Energy× 10^{-2} (eV)
200	29.36
400	25.38
600	22.23
800	22.09

Table (4.10): The activation energy for 10 wt. % NaI

Frequency (kHz)	Activation Energy× 10^{-2} (eV)
200	27.83
400	23.34
600	22.08
800	21.15

Table (4.11): The activation energy for 15 wt. % NaI

Frequency (kHz)	Activation Energy× 10^{-2} (eV)
200	19.23
400	17.71
600	16.56
800	16.22

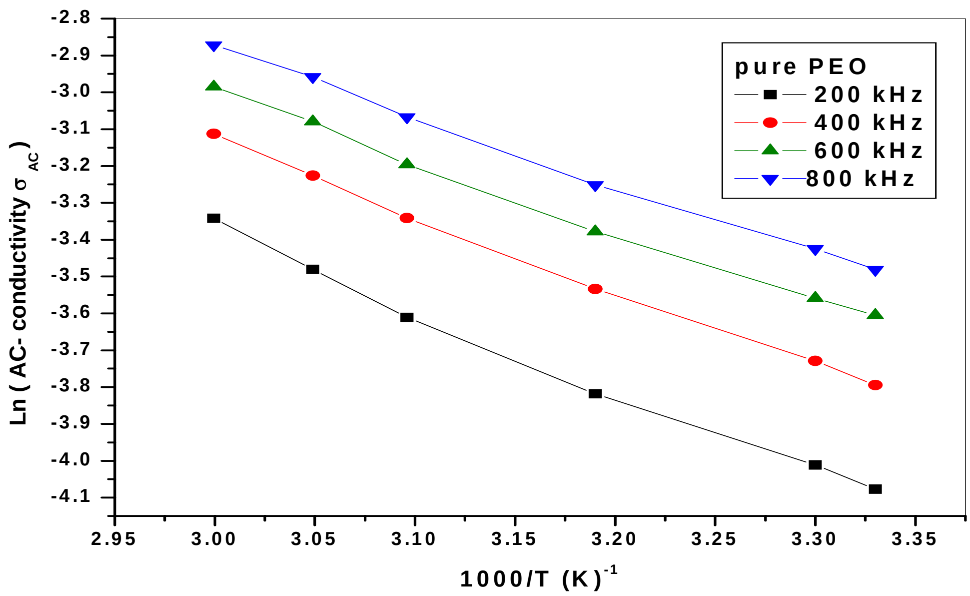


Figure (4.32): Variation of Ln (AC-conductivity) with (1000/T) for neat PEO

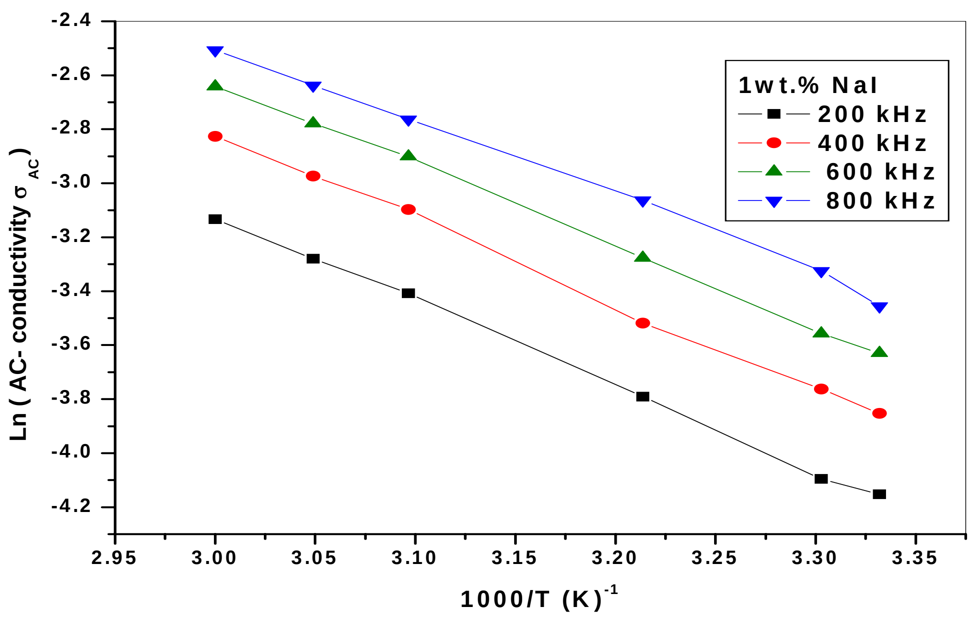


Figure (4.33): Variation of Ln (AC-conductivity) with (1000/T) for 1 wt. % NaI

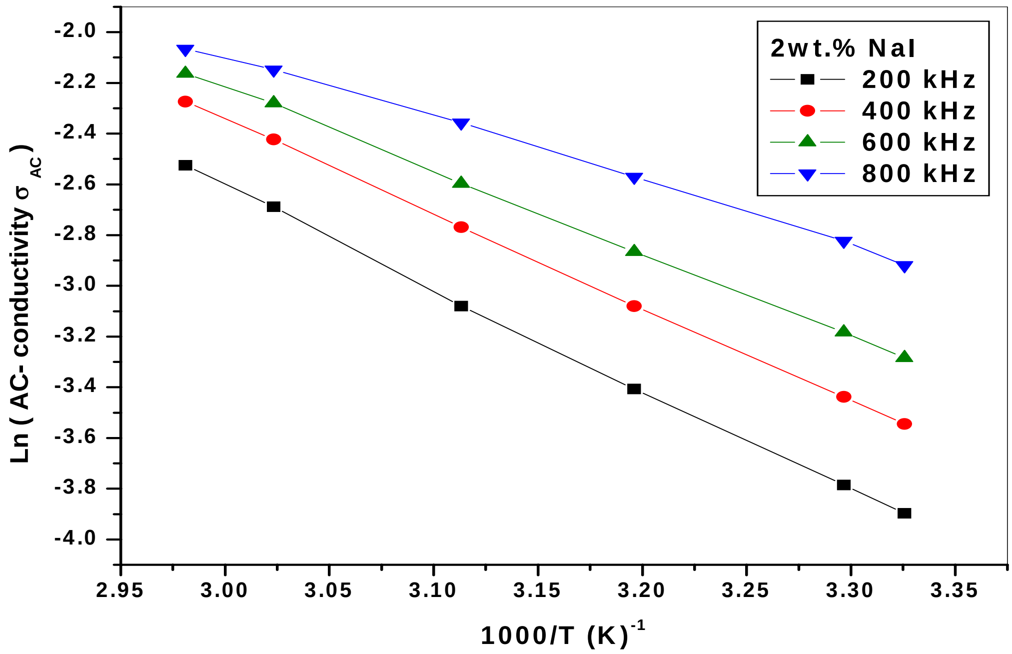


Figure (4.34): Variation of Ln (AC-conductivity) with (1000/T) for2wt.%NaI

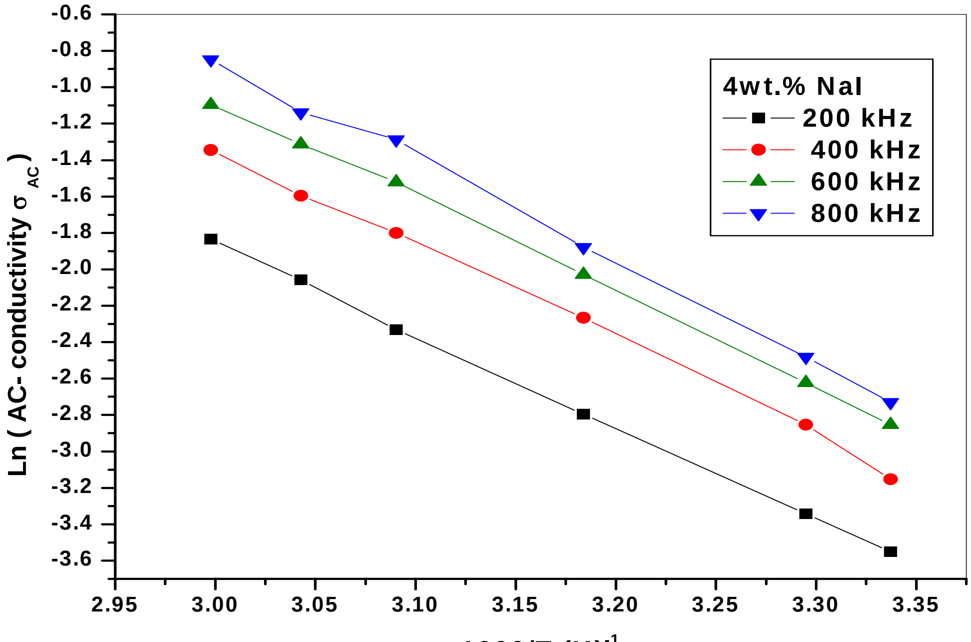


Figure (4.35): Variation of Ln (AC-conductivity) with (1000/T) for 4 wt. % NaI

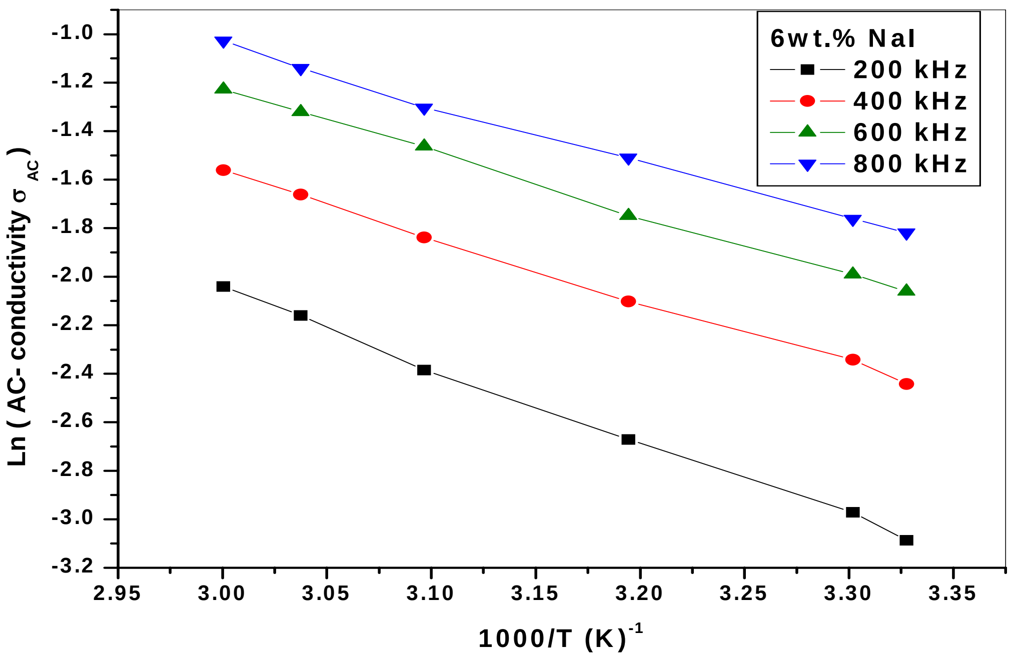


Figure (4.36): Variation of Ln (AC-conductivity) with (1000/T) for 6 wt. % NaI

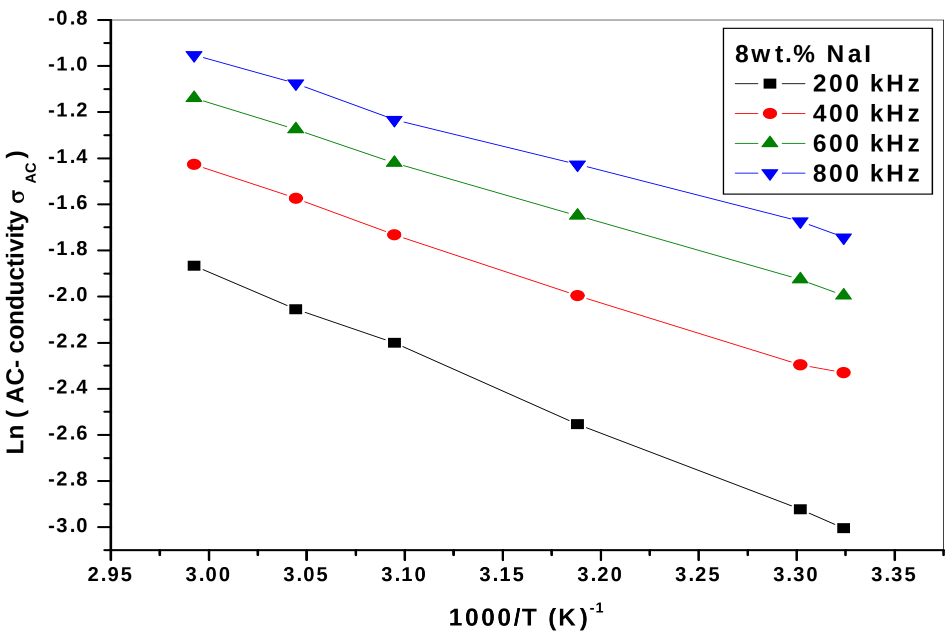


Figure (4.37): Variation of Ln (AC-conductivity) with (1000/T) for 8wt. % NaI

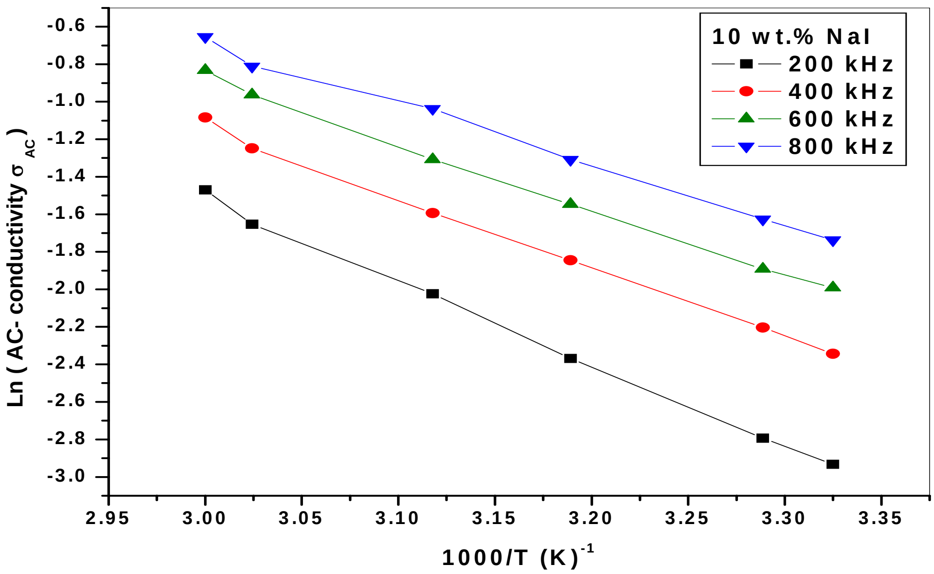


Figure (4.38): Variation of Ln (AC-conductivity) with (1000/T) for 10wt. % NaI

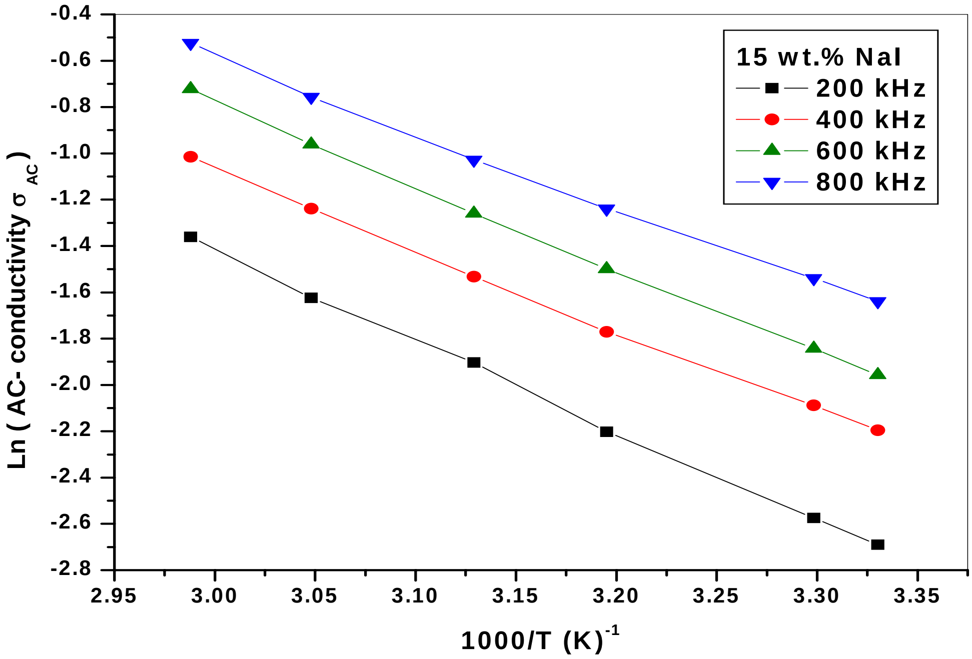


Figure (4.39): Variation of Ln (AC-conductivity) with (1000/T) for 15wt. % NaI

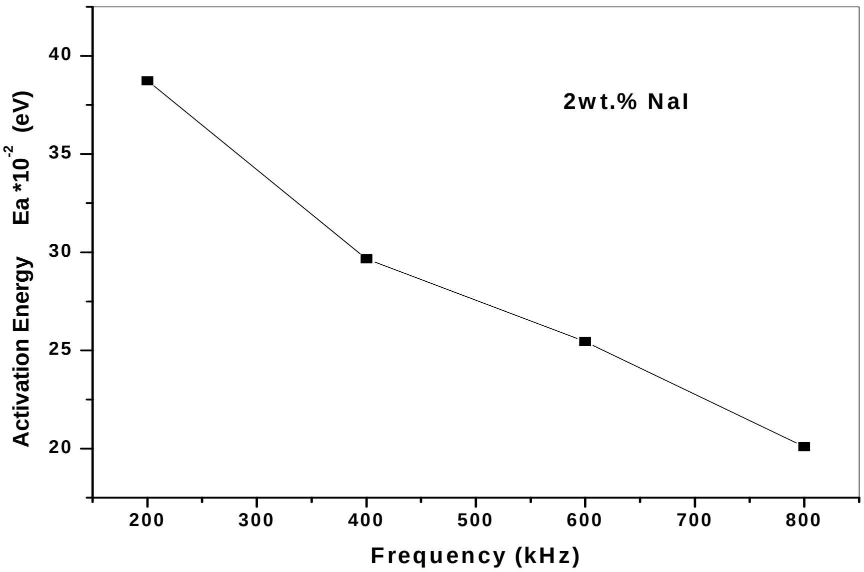


Figure (4.40): Variation of activation energy (E_a) with frequency for 2wt.% NaI composite.

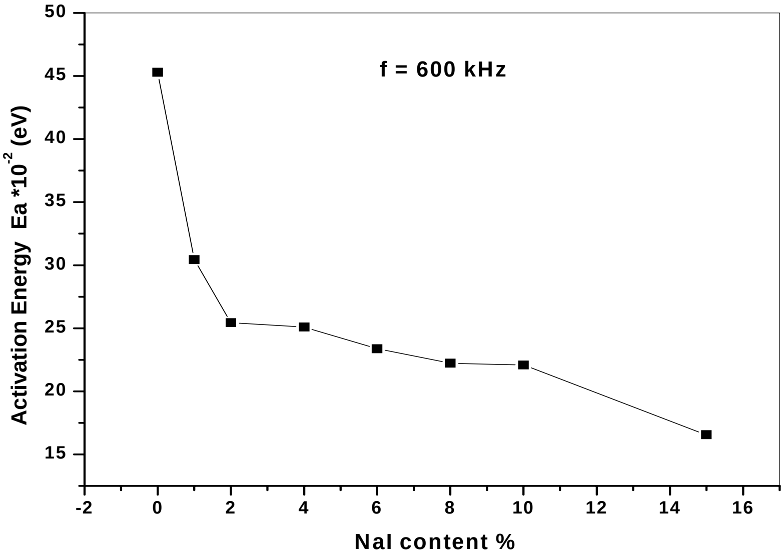


Figure (4.41): Variation of E_a with NaI content at 600 kHz

4.3 Thermal conductivity results

The thermal conduction in solid polymer electrolytes is produced by lattice vibration waves (phonon) and ions transport (as major contributors) and from free electrons and impurities existing in their structure. Measurement of the thermal conductivity of polymeric materials is difficult since its value is relatively small and in the range (0.2-0.4 W/m°C). For polymeric materials, energy transfer is accomplished by vibration and rotation of the chain molecules. The magnitude of the thermal conductivity depends on the degree of crystallinity: polymer with a high crystalline and orded structure will have a greater conductivity than the equivalent amorphous material. This is due to the more effective coordinated vibrations of the molecular chains in the crystalline state. The thermal conductivity is so sensitive to the measuring conditions, physical and chemical structure of the polymer composite. The growing needs for materials to be used in thermal applications lead to the design of new composite materials with appropriate combination of selected polymeric matrices and suitable fillers. Polymers are often used as thermal insulators because of their low thermal conductivities, where the free- electron concentrations are low and phonon conduction predominates.

The thermal conductivity (k) for the eight electrolyte composite samples with different NaI concentration was measured in temperature range from 27 ºC to 60 ºC and calculated from equation (2.51). No higher temperature measurement were performed since the melting temperature for PEO is about 65 ºC .

Figure (4.42) shows comparative graphs of thermal conductivity for eight types of composites. It can be seen that the thermal conductivity (k) increases slightly with

increasing temperature. In case of raising the temperature, phonons, ions, electron, and impurities are activated and thus enhancement in the thermal conductivity is produced.

Figure (4.43) shows the variation of thermal conductivity with NaI concentrations. It can be seen that the thermal conductivity increases with increasing the concentration of the NaI filler content. Thus dispersing NaI phase in PEO matrix enhances the electrolyte thermal conductivity and lowers its thermal resistance, which may be useful to thermal performance applications. Thermal conductivities of the doped PEO increase with increasing the concentration of the dopants. The increase may be due to compactness provided by increase in dopants concentration which increase the heat transfer through phonons diffusion [T.U. Onuegbu, Ph.D.; A.U.G. Okeke, M.Sc.; and U.E. Ekpunobi, Ph.D. , 2010]]

Table (4.12) includes observed values of the thermal conductivity (k) and resistivity (r) for the electrolyte composites, k is about 0.14 (W/m. ºC) and increases to about triple value of 0.50 (W/m. ºC). Thus the NaI electrolytic filler has large effect in enhancement the thermal conduction. Table (4.13) shows a comparison between the electrical and thermal conduction behaviors of the prepared thin films of PEO/NaI solid electrolytes as a function of NaI content. Both the electrical conductivity and thermal conductivity increase with increasing the dispersed NaI phase.

Fitting the observed increase in the thermal conductivity of the composites with the filler volume fraction (figure 4.44) exhibits a linear dependence which is in agreement to that reported by Agrawal et. al. of their measurements on the thermal conductivity of styrene-butadiene [A. Agrawal, N. S. Saxena, G. Mathew, S. Thomas, Kanan B. Sharma,2000].

Table (4 .12): Thermal conductivity , thermal resistivity and thermal resistance values at (T= 30 ^{o}C)

Polymer electrolyte composite	Thermal conductivity(k) (W/m.^{o}C)	Thermal resistivity (r) (m. ^{o}C/W)	Thermal resistance × 10^{-4} (R) (m^2. ^{o}C/W)
Pure PEO	0.14	7.41	5.19
1 wt.% NaI	0.146	6.85	4.79
2 wt.% NaI	0.150	6.67	4.66
4 wt.% NaI	0.153	6.55	4.57
6 wt.% NaI	0.21	4.84	3.33
8 wt.% NaI	0.27	3.70	2.59
10 wt.% NaI	0.38	2.64	1.84
15 wt.% NaI	0.52	1.94	1.35

Table (4.13): Results correlation between the electrical and thermal conductivities.

Polymer electrolyte composite	Thermal conductivity(k) (W/m.^{o}C)	Electrical conductivity(σ_{AC}) × 10^{-6} $(ohm.m)^{-1}$
Pure PEO	0.14	0.02
1 wt.% NaI	0.146	0.03
2 wt.% NaI	0.150	0.05
4 wt.% NaI	0.153	0.08
6 wt.% NaI	0.21	0.14
8 wt.% NaI	0.27	0.15
10 wt.% NaI	0.38	0.16
15 wt.% NaI	0.52	0.19

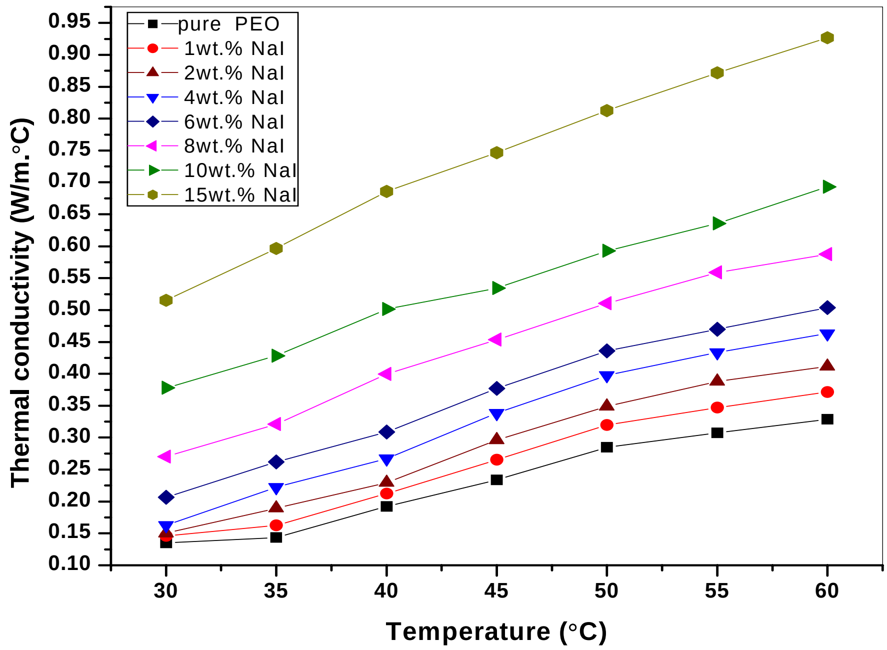


Figure (4.42): Variation of thermal conductivity with temperature for PEO/NaI composite

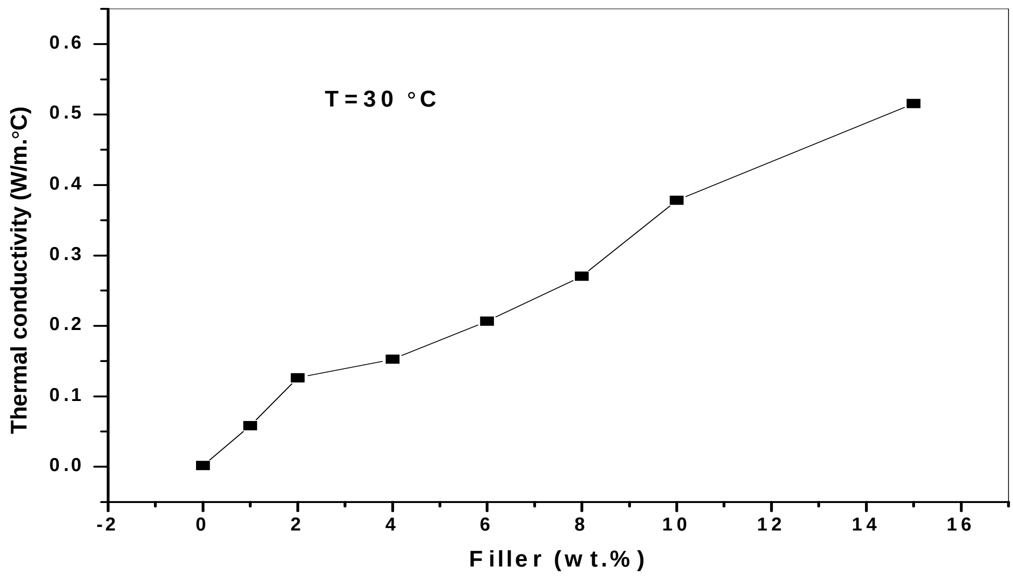


Figure (4.43): Variation of thermal conductivity with NaI Concentrations

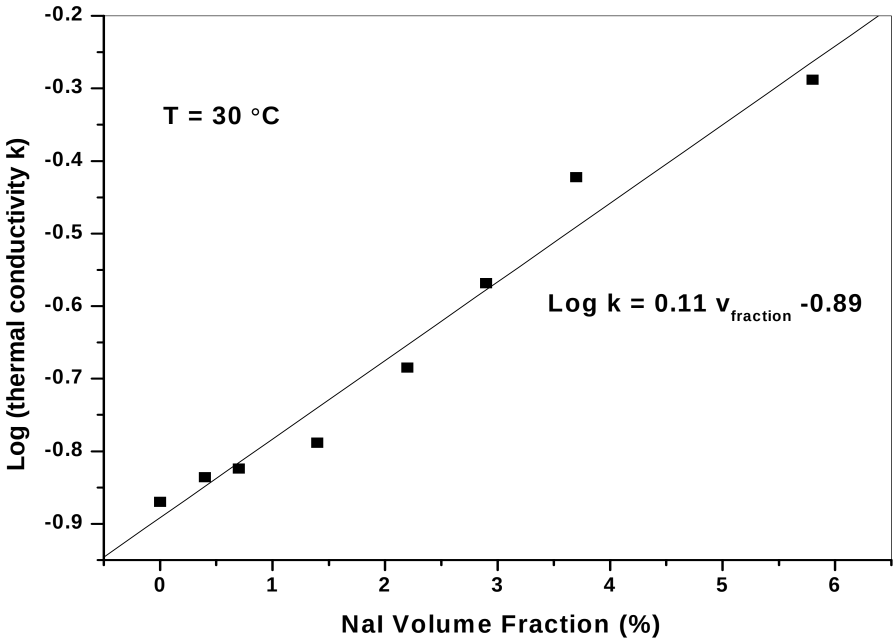


Figure (4.44): Agrawal model of thermal conductivity versus composites volume fraction

4.4 Lorenz Number Determination

Lorenz number is a thermoelectrical parameter characterizing the effect of temperature on both the thermal and electrical conductivities of a solid. In solid state physics, it has a constant value for metals at room temperature (Kittel, 2007).

The Wiedemann-Franz law links the electrical conductivity, $\sigma(T)$, and the thermal conductivity k (T), of a substance by means of the relationship (Kumar and Prasad, 1993):

$$L = k / \sigma T \quad (W.ohm/K^2) \tag{4.9}$$

where T is the absolute temperature and L is the Lorenz number.

Figure (4.45) shows the variation of Lorenz number with filler concentration. It was found that the Lorenz number increases with increasing NaI concentrations. The reason that the Lorenz number (L) increases with the NaI concentration refers to the difference in the rate of increasing of σ_{ac} and the enhancement of the thermal conductivity (k) with the filler content as shown in figure (4.18) and compared with figure (4.42).

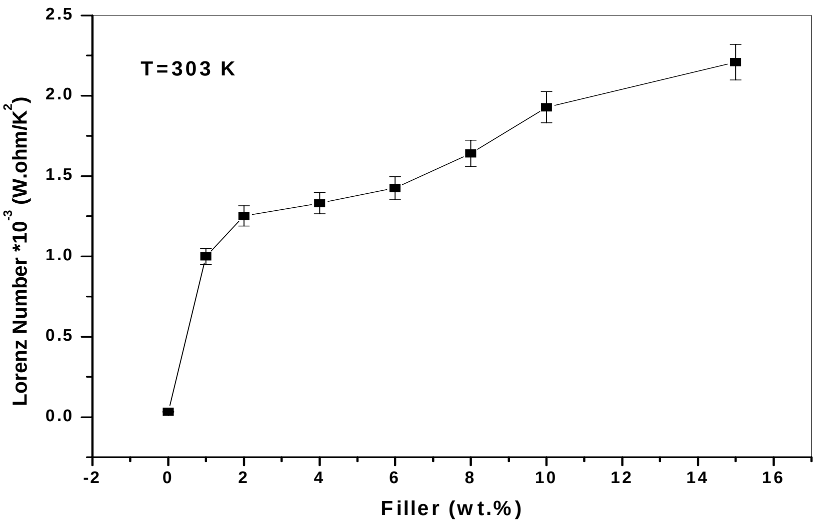


Figure (4.45): Variation of Lorenz number with NaI concentration

CHAPTER FIVE
CONCLUSIONS & FUTURE WORK

5.1 Conclusions

The optical, electrical, and thermal properties of PEO/NaI electrolyte composites with different NaI concentrations were studied. By analyzing the results obtained, one can conclude the followings:

1] Analysis of the optical energy results indicate that the electrons transition is direct in k-space.

2] The optical energy gap (E_{opt}) value decreases with increasing NaI concentration.

3] The band energy tails (ΔE) increases with increasing NaI concentration.

4] The calculated refractive index and dielectric constants of composites increase with NaI particles content in the optical wavelength range.

5] Impedance was found to decrease with increasing frequency, temperature, and filler concentration.

6] The dielectric constant (ε') and the dielectric loss (ε'') of the composites increase with NaI concentration and decrease with frequency.

7] The AC conductivity (σ_{ac}) increases with frequency, temperature, and NaI concentration.

8] The relaxation time (τ) and the activation energy showed variations with NaI content, temperature and frequency.

9] The universal power law of the AC conductivity dependence on frequency and temperature is satisfied.

10] Thermal conductivity increases with both temperature and NaI concentration in the composite.

11] The Agrwal's model fits the increasing of the thermal conductivity with the filler concentration.

5.2 Future Work

I suggest more researches can be done as:

1] The DC electrical conductivity as a function of temperature.

2] The electrical properties in wider frequency range (8 -12 *GHz*).

3] The electric and dielectric properties as a function of frequency at low temperatures.

4] The thermal conductivity at low temperatures.

5] The mechanical properties as yield stress, and viscoelastic behavior.

6] The dependence of the glass transition temperature on NaI concentration.

7] Deeper study of the composites morphology.

8] Studying the dynamioc mechanical behavior of the prepared composites.

5.3 Publications

1] "A Study on Optical Absorption and Constants of Doped Poly(ethylene oxide) ".

R.S. Al-Faleh and A.M. Zihlif. **Physica B**: 406 (2011) 1919- 1925.

2] " Electrical and Thermal Characterization of Doped Poly(ethylene oxide) ".

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الخصائص الفيزيائية للمبلمر بولي ايثيلين اكسيد المطعم بيوديد الصوديوم

إعــداد
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مـــلـــخّـــــــــص

يتضمن هذا العمل البحثي دراسة الخصائص الضوئية والكهربائية والحرارية لمتراكب مبلمر مكون من البولي ايثيلين اكسيد المطعم بيوديد الصوديوم بتراكيز مختلفة درست الخصائص الضوئية للمتراكب ضمن مدى طول موجي (300nm- 800 nm) باستخدام المطياف الضوئي.وجد أن قيم فجوة الطاقة وعرض ذيل مستويات الطاقة الموضعية تتغير بتغير تركيز يوديد الصوديوم في هذا المتراكب الاكتروليتي.

تضمن البحث دراسة الخصائص الكهربائية للمتراكب عند درجات حرارة تتراوح من (27Cº – 60Cº) باستخدام تقنـــية الممـــانعة الكهربائية المتناوبة في مدى التردد (30 kHz –5 MHz) . ومعرفة تأثير تردد المجال الكهربائي المسلط على العينة، وتأثير تركيز يوديد الصوديوم على العازلية والموصلية المتناوبة. وقد لوحظ أن الموصلية المتناوبة تزداد بازدياد التردد ودرجة الحرارة و تركيز يوديد الصوديوم في المتراكب، بينما يزداد ثابت العازل بزيادة درجة الحرارة و تركيز يوديد الصوديوم، ويتناقص بازدياد التردد .

كما درست الخصائص الحرارية لهذا المتراكب، ووجد أن الموصلية الحرارية تزداد قليلا" مع كل من درجة الحرارة وتركيز يوديد الصوديوم في المتراكب. كذالك تضمنت الدراسة تطبيق بعض النماذج الرياضية على النتائج التجريبية للخصائص الفيزيائية المدروسة. حيث كانت درجة التطابق مقبولة بين النتائج التجريبية والنظرية.